INTENSIFICATION OF BIODIESEL PRODUCTION FROM JATROPHA ON IN-SITU TRANSESTERIFICATION

By

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Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

Intensification of Biodiesel Production on In-situ Transesterification of Jatropha seeds: Effect of Ultrasonication & Heterogeneous Catalyst

By

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A project dissertation submitted to the

Chemical Engineering Programme

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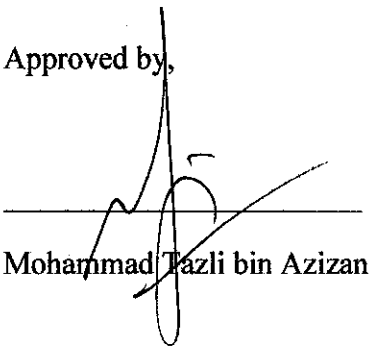
Approved by,



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January 2009

CERTIFICATION OF ORIGINALITY

This is to certify that i am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

ROSFAIZUL BIN ISMAIL

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ABSTRACT

Process intensification is defined as improvement of process mainly reaction by any possible means to increase the overall productivity. This work presents the study of intensification methods that can be applied to biodiesel synthesis using Jatropha seed via in-situ transesterification. Jatropha is selected as the source of the biodiesel due to it inedible properties and high oil contents. The small percentage of acid value in the seeds only required single step transesterification process. The Jatropha seeds will be extracted chemically (in situ) to preserve the quality and getting high yield on instant with transesterification process. Transesterification is a method to reduce the oils viscosity and the best practiced in biodiesel production than other methods. The process can be catalyzed either by acid, alkalis or enzyme. The utilization of biodiesel in replacing the existing diesel from fossil resources, contributes in solving many environment problems. For process intensification, the effect of ultrasonic will be investigated. The method claims to increases the chemical reaction speed by cavitations effect giving sufficient activation energy for the transesterification process. Besides that, the investigation on the effect of heterogeneous catalyst towards the production efficiency will also be performed. All the research and findings obtained will be applied to find the optimum parameters for biodiesel production in lab scale.

CHAPTER 1: INTRODUCTION

1.1. Background of study

The usage of energy sources has undergone a series of evolution. From the beginning of history up to industrial revolution around 18th century, mankind's use of energy relied only on one muscular and biomass sources. Most work forces were provided by manual labor and animals, while the biomass energy mainly from wood was use for heating and cooking. Other sources of energy such as windmills and watermills were present at that time, but the contribution was very small in effect. Due to industrial revolution at the mid of 19th century, major shift of energy sources from coal is introduced. The energy from coal initially for steam engines, the usage later on increases for power plant as well. As the 20th century began, the major reliance was on coal, but a gradual shift towards higher energy contents sources like oil began. This second energy resource shift officially used worldwide in the era of the internal combustion engine and oil powered ships. In the late of 20th century, the world economy starting to depends heavily on the internal combustion engine and supporting industries which later on emphasis petroleum products as the main provider of energy. As the technologies develop and technical expertise increased, mankind was able to obtain more efficient sources of fossil fuels, mainly natural gas. (Tickel,2003).

Nowadays, the 20th century energy resources technologies of polluting petro fuels starting to show gradual obsolescence and shifting to more efficient petro fuels such as natural gas. The concerns of environment effects and petrol fuel depletion have led to stride for new renewable energy sources. The next generation energy sources are speculated to be the usage of hydrogen cells, and other is biodiesel. As hydrogen cells technology is still new, parallel development of important multiple energy sources should be working on to ensure energy demand is well cater.

Biodiesel starts to show significance importance concerning the fact that fossil fuel will eventually come into depletion. The need of non-depletion energy sources concern has urged researches to stride for renewable fuels technology. One of the technologies is biodiesel.

The advantages of using biodiesel technology as wrote and discussed by J.Tickel in his book of biodiesel (2003) and documentation provided by National Biodiesel Board are:-

a) *Infinite supply of renewable energy*: Biodiesel comes from plants which can be constantly grown and replenished as desired. Compared to fossil fuels which took 40 million years to produce, biodiesel can be produce for couple of months.

b) *Carbon neutral properties*: Instead a system where hydrocarbons are extracted from the ground and carbon dioxide is emitted into the atmosphere, the use of biodiesel promotes the cycle where hydrocarbons are grown and carbon dioxide is adsorb from atmosphere to produce oxygen.

c) *Better lubricating properties:* All diesel injection equipment has some reliance on diesel as lubricating system. High lubricating fuel will provide reduced wear and higher component life. The need to remove sulfur and aromatics levels in fossil fuel technology has inadvertently reduced the compounds that provide lubricity to the fuel.

d) *Safe and easy handling*: The biodiesel can be used as it or blend with the fossil fuel diesel. The higher flash point properties of biodiesel made the fuel easier to be handling especially in transportation.

e) *Environmental friendly:* Biodiesel is non-toxic. Study by Ahmed et al shown biodiesel is biodegraded up to four times faster than petroleum diesel fuel. The fuels exhausted is free of lead, sulfur dioxide, halogens, and has reduced particulates unburned hydrocarbons, carbon monoxide, and carbon dioxide.(Korbiz, Werner, 1993)

Biodiesel can be derived from agriculture sources by several methods, most popular and widely used method is transesterification of the refined vegetable oils such as soybean, sunflower and palm oil. The production of biodiesel from vegetable sources like soybean and rape seed have long been practiced by developed countries such as US and Europe continents. Awareness of concern between food and fuel has soon made the interest of using non-edible sources of

vegetable oil as feedstock in biodiesel production growing rapidly. The Jatropha seed is later recognized as one of the potential alternative feedstock for the biodiesel production.

The tree is plant commercially in India. The seed of the tree is seen to be the perfect biodiesel crop. It can be grown in very poor soils condition and continually generating good soil as it growth, as well as drought and resilient to pest. In addition, there is up to 40% oil content in the seeds made it almost perfect source of biodiesel. The process of deriving biodiesel from the seed can be done by transesterification of which is the method that will be used by the author in the project. The process is achieved by reacting triglycerides in the seed with alcohol with the presence of acid or alkaline catalyst. (Naoko Ellis et al, 2006)

1.2. Problem statement

In the upcoming years, the price of fossil fuels such as diesel and gasoline is expected to become too expensive for most people. The report by Peter Beaumont and John Hooper (2004) mentioned that it is not impossible that fossil fuel will become too expensive, as it did during the oil shocks of the 1970s. The fact of "oil shocks" or a sudden and sharp price increase in oil follow by a decrease in availability also supported by Campbell, the author of "The coming oil crisis". He insisted the halfway point of diesel production from fossil fuel began to narrow is the most crucial time in economy. Low availability and continuous demand will forces the oil prices to increase significantly. The problem however can be solved by gradually replacing the fuel sources with the renewable sources. This is where the biodiesel production from non-depleting sources starts to take the role.

Biodiesel can be produced by using vegetables oils such as soybean, canola oil, sunflower oil and animal fats. However the use of animal fats in commercial biodiesel production is not practical for the limited supply of the animal fats. It is also not efficient to raise animal for the fats. Initially, waste vegetable oil is use as the sources of oil to produce biodiesel. However, because of the available supply is drastically less than the amount of petroleum-based fuel that is burned for transportation and home heating, biodiesel start to be produce using fresh vegetable oil from farm. This in turn led to the issue of conflict between food and fuels. The increased usage of edible vegetable sources is a major concern that will decrease food sources

which eventually increase the food prices. Concerning the matters, the sources of new non-edible source which is Jatropha carcass plant is introduced.

Raw triglyceride oils from Jatropha seeds and other vegetable sources have properties similar to fossil-based diesel fuels. However long term operation by directly using raw vegetables oils may causes numerous problems including injector coking and contamination of the tank. These problems are primarily the result of the high viscosity of the triglyceride oils as compared to fossil-based diesel fuels. Increased viscosity affects fuel injection adversely. The transesterification process is one useful method to reduce the high viscosity of triglyceride oils. In this process, the long fatty acid chains are removed from the glyceride molecule by reacting with alcohol and a catalyst. The concern is this process will proceed either exceedingly slow or not occurring at all. In order to solve this, commonly heat as well as homogenous acid or base catalyst is used to increase the reaction. Compare to acid, base catalyst give faster reaction and better yield. The removal of base catalyst at the end of the process is cumbersome. Apart from that, the waste produced by production of biodiesel using homogenous base catalyst often environmentally toxic. To solve this matter transesterification of the oils using heterogeneous type catalyst will be investigated.

Conventionally, vegetable oil is pre-extracted from the seed prior to transesterification using hexane or a mechanical press. In addition to slow reaction time in transesterification, there is also addition in time to mechanical extracting the oil. In-situ transesterification is therefore introduced to solve this matter. The uses of batch reactor in the process also hinder the full efficiency of biodiesel production. Most common method in biodiesel production is the one step or two steps batch transesterification process. Batch processes have suffered several disadvantages to compare to continuous process because batch processes require larger volume resulting in higher capital investment. Apart from that, biodiesel production also suffers from slow reaction rate and high molar ratio of alcohol usages to achieve high biodiesel conversion. This high amount of alcohol usages and slow reaction however can be fix by the application of ultrasonic cavitations. Ultrasonic cavitations provided the activation energy need by biodiesel production by giving better mixing.

The paper will investigate the use of heterogeneous base type of catalyst, and other intensification technology application suitable such as continuous reactor or ultrasonic cavitations application.

1.3. Objective of studies

a) *To intensify the biodiesel production by heterogeneous catalyst and ultrasonication.*

Come out with researches to intensify the in situ biodiesel production, whether to increase the rate of reactions, the yield, lowered production time and more economical. This is achieved by heterogeneous catalyst and ultrasonic water bath application.

b) *To analyze the effect of using different type of catalyst*

To build a comparison data between the types of catalyst, especially heterogeneous catalyst and to further investigate the best catalyst.

CHAPTER 2: LITERATURES REVIEW

2.1 World energy demand

Currently oil prices are higher than theoretically resulting of fears over supply shortages. According to "The age of easy energy is over" article by Thilo Kunzemann (2007) which containing interview with Allianz global foreign investor, Christopher Wheaton, discussing about the energy demand trend. Despite a weak U.S. economy, where oil demand is down about two percent in 2007, the consuming of oil rate still high. Wheaton suggested, in order to decrease the oil prices, there is a need to having high prices of oils. The high prices will force the demand to decrease and in turn causing the world production producing more oil than it is consumed. The age of easy energy consumption is over. Fossil fuel is getting harder and more expensive to extract than before. The increasing amount of oil coming from deep, offshore oil fields need higher development costs rising operation cost as well.

Another option to cater the energy demand is by investing in nuclear energy, because there are not enough alternatives to meet energy demands apart from biodiesel. The concern is that investment in nuclear energy takes longer and is more expensive than the budget allows. However, there is a certain amount of speculation within the renewable energy market. All renewable sources are interesting in a different way. Wind and hydropower have low operating costs, but they are already being exploited in terms of potential sites. Solar or geothermal have higher costs, but much more growth potential. Biodiesel development stands up out of the options as another potential energy source to cater the world energy demand, not only meet the need of energy usages but also as transportation usages. Optimization of this renewable energy sources is a must to solve the energy demand issues (Source: "The age of easy energy is over" article by Thilo Kunzemann, 2007).

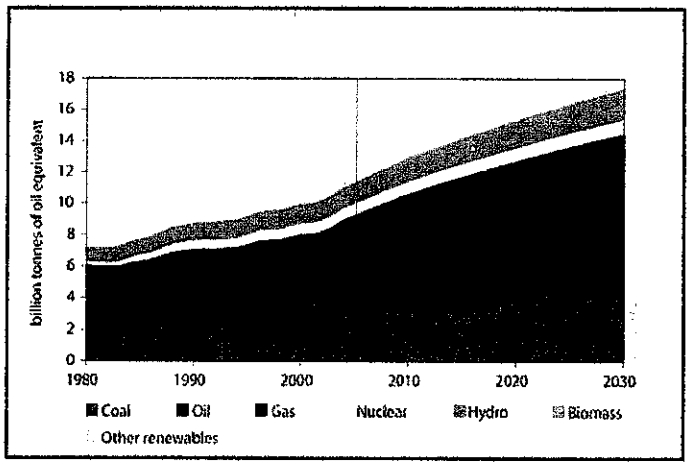


Figure 2.1: World primary energy demand in reference scenario (source: IEA 2007)

The International Energy Agency (IEA) in latest analysis (2007) projects that world's primary energy needs will grow by 55 percent between 2005 and 2030. Fossil fuels will remain the dominant source of primary energy, accounting for 84 percent of the overall increase in demand by 2030. As can be seen in Figure 2.1, the demand is forecasted to increased gradually over the period with renewable energy demand predict to increase up to 50% between 1980 and 2030. The fossil fuel demand is still predicted to contribute to the largest value to the world energy consumption.

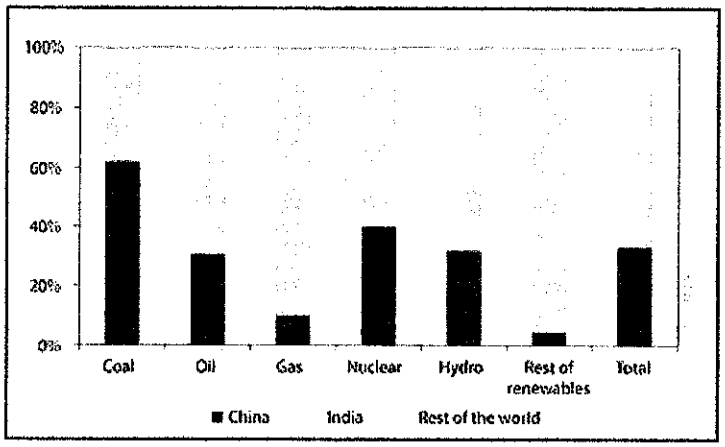


Figure 2.2: Increase in world primary energy demand in reference scenario as 2005 – 2030 (sources: IEA 2007)

In term of increasing percentages of energy demand, developing countries will contribute 74 percent of the increased in global primary energy as predicted by the IEA (Figure 2.2). Big countries like China and India alone will account for 45 percent of this increase. OECD (Organization for Economic Cooperation and development) countries account for one-fifth. In aggregate, developing countries make up 47 percent of the global energy market in 2015 and more than half in 2030.

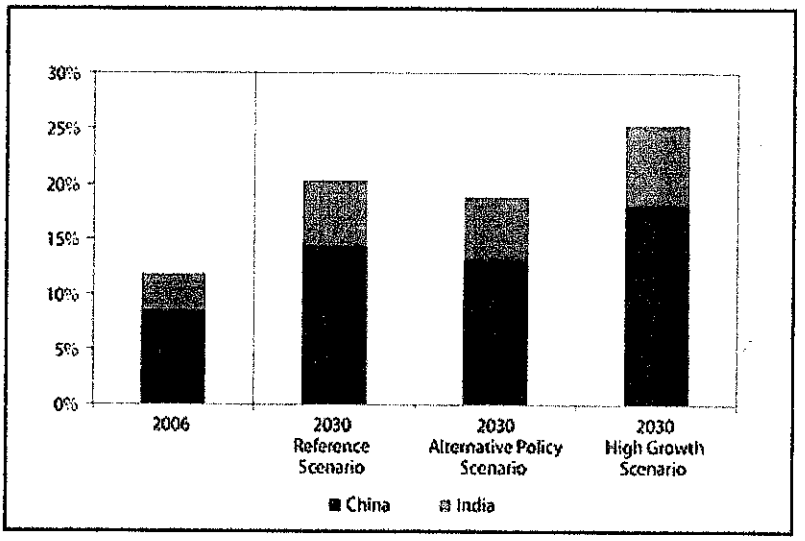


Figure 2.3: Shares of China and India in world demand by scenario (sources: IEA 2007)

In the IEA's reference scenario, big developed country represented by China's and India's combined oil imports surge from 5.4 million barrels per day in 2006 to 19.1 million barrels per day in 2030. The value is more than the combined imports of Japan and the United States today.

From the world demand analysis references, it is concluded that the demand of the energy will continues to grow, especially to large population countries like China and India. At the same time, more demand lead to increasing the consumption rate, eventually the limited resources will start to decline. The shortage of oil which leads to social and economic disruption is inevitable. Only development of sufficient alternative fuels will solve this matter.

2.2 Oil price hike

The demand and economy are very strong in effect, especially to product which is limited in availability. The same goes to fossil fuel. Global energy consumption growth remained robust in 2007, driven by above-average economic growth. Despite continued high prices, OECD countries are showing the most significant reaction to continued high energy prices.

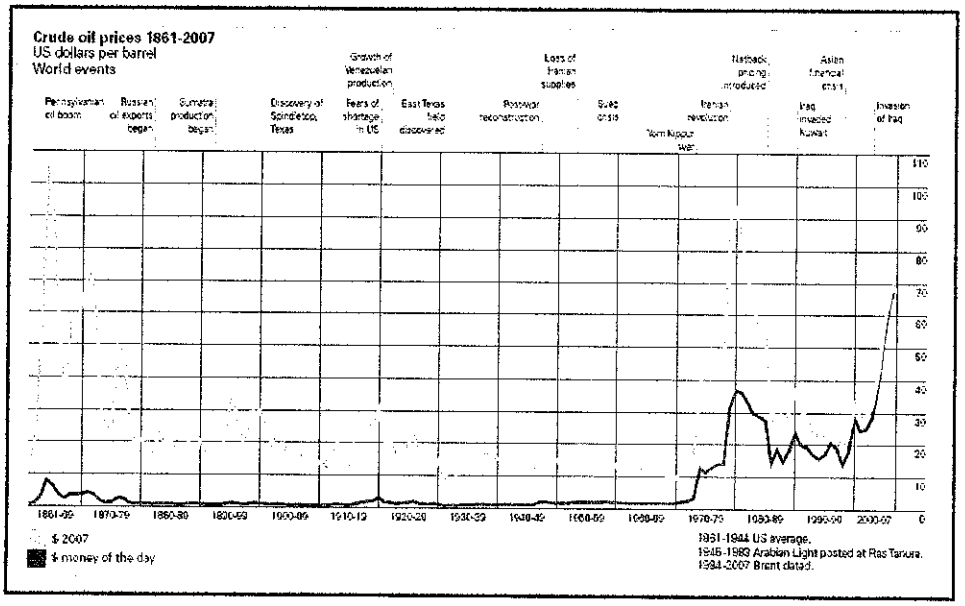


Figure 2.4: Crude oil prices 1861-2007 (Sources: BP Statistical Review: June 2008)

Figure 2.4 shows the trend of crude oil prices from 1861 to 2007. As can be seen, the prices of the crude oil from 1880 to 1970 can be considered as fluctuating stably. The prices increase steeply at the end of 1980 but later on gradually decrease at 90's. The start of new millennium shows the gradual increase of the crude oil prices until 2007. The data suggest the trend of the prices oil for upcoming years. As discuss previously, the increasing demand of energy demand particularly fossil oil sources is undeniable will resulting further increase of the prices of crude oil for upcoming years. Thus, renewable sources of energy to replace some portion of crude oil consumption and usage will also influence of the curves to be more slanting upward or downward.

2.3 Food versus fuel

One of the past century achievement is no doubt to be the enormous expansion of food production and technology, which has virtually solve the starvation problems in advanced countries and has made huge gains from it especially in poor countries. Since 1961, world population has increased 112%, meanwhile, global production is up 164% for grains and almost 700% for meats (Samuelson, 2008).But the world food system is concerned undergoing a radical break. During the past year, prices of basic grains and oilseeds, particularly corns and soybeans have soared. Higher grocery prices obviously make it harder to achieve economic growth and low inflation simultaneously. The truly grave consequences involve poor countries, where higher prices threaten more hunger and malnutrition.

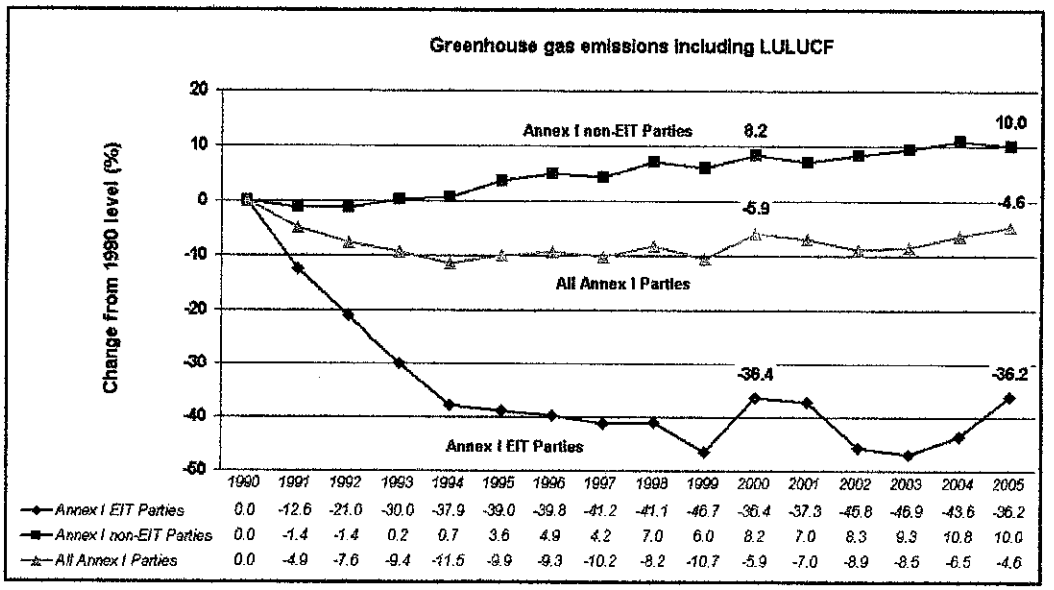
In United States, the extra demand for grains to make biofuels which heavily influenced by government tax subsidies and fuel mandates, has pushed prices dramatically higher. Since 2000, the share of the U.S. corn crop devoted to ethanol production has increased from about 6 percent to about 25 percent and it is increasing (Samuelson, 2008). The fact is not only applied to the corn crop. Other sources of edible biodiesel also could suffer from the same prices increment. The clear example can be seen in Asia country particularly Malaysia is the use of palm oil. The use of palm oil as biodiesel sources might not only disrupts the market price for cooking oil, it also decreases the availability to cater the demands.

However the problem might have been exaggerated. Terry Francl a senior economist in his journal of "Fuels versus Food: Is it Rhetoric or Reality?" said, the relation of high consumption edible agriculture sources for biofuels production is still vague. Apart from U.S increasing prices, other food sources like meat also having the same price increasing. The fact that there is no relation between corns and meats production has made the price increasing not necessary resulting from biodiesel production consumption. However, to be save biodiesel production from inedible sources should be favor. The use of Jatropha seeds as the alternative sources of biofuels production is highly recommended because not only it is inedible, the plant also can be find in abundant and act as natural fertilizer for wasteland.

2.4 Climate changes

Over a decade ago, the United Nations Framework Convention on Climate Change (UNFCCC) is formed and joint by most countries as an international treaty. The initial formation objectives are to put awareness among the countries of what can be done to reduce global warming and to cope with inevitable temperature increases. Now, the ultimate objective of the UNFCCC is to achieve stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. The estimation of the levels of greenhouse gas (GHG) emissions and removals is an important element of the efforts to achieve this objective. (Source: UNFCC website).

In 2005, a number of nations approved an addition to the treaty which is Kyoto Protocol. The Kyoto Protocol is an international and legal binding agreement to reduce greenhouse gas emissions worldwide, adopted in Kyoto, Japan, on 11 December 1997 and entered into force on 16 February 2005. The major distinction between the protocol and the convention is that while the convention encouraged the industrialized countries to stabilize green house gas emissions, the protocol commits them to follow. (Source: UNFCC website).



	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
Annex I EIT Parties	0.0	-12.6	-21.0	-30.0	-37.9	-39.0	-39.8	-41.2	-41.1	-46.7	-36.4	-37.3	-45.8	-46.9	-43.6	-36.2
Annex I non-EIT Parties	0.0	-1.4	-1.4	0.2	0.7	3.6	4.9	4.2	7.0	6.0	8.2	7.0	8.3	9.3	10.8	10.0
All Annex I Parties	0.0	-4.9	-7.6	-9.4	-11.5	-9.9	-9.3	-10.2	-8.2	-10.7	-5.9	-7.0	-8.9	-8.5	-6.5	-4.6

Figure 2.5: Greenhouse gas emissions including LULUCF (Source: UNFCC Website)

Figure 2.5 shows the latest data of percentage changes of greenhouse gas emission (Carbon dioxide, Methane, Nitrous oxide, Perfluorocarbons, Hydrofluorocarbons, Sulphur hexafluoride) from 1990 to 2005 from the UNFCC convention, the data covers the Land Use Land Used Change and Forestry (LULUCF) provided by the team countries. EIT refer to Economies in transition program under the UNFCC. From the data, shown that only non-EIT annex I country has gradually increased in gas emission percentages. Other solution to decrease the percentage of gas emission particularly carbon dioxide and Hydrofluorocarbons is none other than implementation of biodiesel as new sources of alternative energy.

2.5 Biofuel and biodiesel

2.5.1 The Overview

Biofuel is defined as liquid fuel derived from biomass and is distinguished from fossil fuels which are derived from long dead biological material. Theoretically, biofuels can be produced from any (biological) carbon sources, the most common sources is photosynthetic plant. The sun is the source of all energy on Earth. Every day, enough source of all energy in the form of sunlight hits the earth. Most of the energy turns into heat and some of it absorbed by plants by photosynthesis mean. Plants transform solar energy into chemical energy in the form of hydrocarbons. Whereas fossil fuels came from plants which grew millions years ago, biofuels come from plants which are constantly grown and replenished. Biofuels are most commonly used to power vehicles and cooking stoves. The industries are expanding in Europe, Asia and America.

The possibility of biofuels in offering energy production without a net increase of carbon into the atmosphere has caught the attention of many. This is because the plantation of plants used in the production of the fuel removed CO_2 from the atmosphere as it grows. This is unlike fossil fuels which return carbon that was stored beneath the surface for millions of years back into the atmosphere as it burns. Therefore, in theory biofuel is more carbon neutral and less likely to increase atmospheric concentrations of the greenhouse gases. In addition, the use of biofuel also reduces the dependence on petroleum sources and enhances energy security. (Sources: Smart Way and Go website)

Basically, there are two common methods in producing biofuels. One is to grow crops high in sugar contents or glucose like sugar cane or corn and then to use yeast fermentation to produce ethanol. The second is to grow plants that contain high amounts of vegetable oil, such as oil palm, soybean, algae, or Jatropha. When these oils are heated, their viscosity is reduced, and they can be burned directly in a diesel engine, or they can be chemically processed to produce fuels such as biodiesel. Wood and its byproducts can also be converted into biofuels such as wood gas, methanol or ethanol fuel.

Biodiesel produced chemically by reaction between alcohol and vegetable oils or animal fats. It is produced by converting glycerin in the vegetable oil into ester mixture with physic-chemical properties akin to petroleum diesel (José María Cerveró et al, 2008). The ester production conversion process is called transesterification. The transesterification method is the most common way in producing biodiesel. The methods can be run in catalyzed or non-catalyzed system.

Biodiesel produced can be operated in conventional compression ignition-engine. The fuel with high boiling point, low vapor pressure and water immiscible has better lubricating properties than today's lower viscosity diesel fuels. Addition of 0.4% to 5% biodiesel into current diesel can significantly reduce engine wear and increasing the life of the fuel injection by increasing the fuel lubricity (Biodiesel: Cost Effective Lubricity Enhancer, Nopec Corporation, 1997). This proved to be important improvement, especially to equipment that heavily relies on the fuel for its lubrication, such as high pressure injection pumps, pump injectors and fuel injectors. Previous method of diesel lubrication is once worked by sulfur contents. However, when fuel containing sulfur is burned, sulfur dioxide gas which is primary component of acid rain will be produced (Gordon, Deborah, 1991). Thus the use of biodiesel not only provide lubricity for engines performances, it also environmental friendly.

To concluded, biofuel or biodiesel playing significant roles in solving variety international issues which include the mitigation of carbon emissions levels and oil prices stability. Introduction of jatropha as alternative biodiesel feedstocks also solved the issues of food versus fuel conflicts, deforestation and soil erosion. The implementation of biodiesel from biofuel to gradually replace the use of fossil fuels would be among the best measure for many issues.

2.5.2 Characterization of Biodiesel

Characterization of biodiesel can be estimated by the basis of blended biodiesel percentage in the fuel. The test sample variable is ranged between 100 percent biodiesel and 100 percent low sulfur fossil fuel. The fuel contents 100 percent biodiesel is characterize as B100, while the number of "100" indicate the percentages of the biodiesel blended. The characterizations of Biodiesel as study by L.Schumacher et al and J.Tickel are:

a) Density and specific gravity

The density and specific gravity of blended fuel is proportionally increased with every percentage blends of biodiesel into fossil fuel. Fuel injection equipment operates on a volume metering system, hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel. The density also related to viscosity in which the increment of biodiesel density from 848 to 885 g/L will increase the viscosity from 2.8 to 5.1cSt (Demirbas, 2007)

b) Cloud Point and Flash Point

The cloud point and flashpoint of blended fuel is proportionally increased with every percentage blends of biodiesel into fossil fuel. B100 biodiesel having the highest flash point, which indicate the rareness of spontaneously explode under normal circumstances. Thus Biodiesel is easier in storing and transportation.

c) Viscosity

The viscosity of blended fuel is proportionally increased with every percentage blends of biodiesel into fossil fuel. High viscosity is not good for engines, thus proper biodiesel methodology that reduces viscosity is need.

d) Heat of Combustion

The heat of combustion is proportionally decreased with every percentage blends of biodiesel into fossil fuel. B100 biodiesel has approximately 12% less energy to compare with fossil diesel fuel. The reduction of energy in biodiesel is partially offset by a 7% average increase in the combustion efficiency of biodiesel. On average Biodiesel use

results in 5% decrease in torque, power and fuel efficiency. However the performance of most vehicles using biodiesel is not noticeably affected.

e) Lubricity

Between 0.4-5% biodiesel blends or B5 will increase the fuel lubricity significantly. Better lubricity meant better engines wear resistances.

f) Biodegradability and toxicity

B100 biodiesel is as biodegradable as sugar and less toxic than table salt. Studies have shown that biodiesel biodegrade 4 times faster than petroleum diesel.

2.5.3 Benefits of Biodiesel to Malaysia

Biodiesel is not a new technology to Malaysia. The technology of biodiesel is already implemented with the use of Palm oil as the raw sources. The benefits of Biodiesel production particularly using Jatropha as the feedstock of biodiesel are:

a) Mitigating the effects of Petroleum price escalation

Currently, dependency of petroleum sources and outside price has forces the fuel price increment. Cheap alternative fuel from bio sources could help lifting the price burden among diesel user.

b) Efficient utilization of raw materials and area.

The use of raw materials and it's by side components from agriculture sources with high biofuels contents for production of biodiesel will promote efficient utilization of raw materials. By introducing Jatropha, the Palm tree can be utilize to only cater the need of cooking oils production.

c) *Strengthen the economy*

The development of biodiesel industry has job opportunities potential, adding billion incomes to economy each year and decrease the trade deficit by at least 30 percent.

Commercialization of Jatropha tree and plantation also expected to strengthen the economy.

d) Environmental friendly

The uses of biofuels prove to reduce the emissions of greenhouse gases which promote better life quality of the nation citizen.

e) Natural fertilizer

The use of Jatropha promotes natural fertilizer. Jatropha can be intercropped with many cash crops such as coffee, sugar, fruits and vegetables with the Jatropha offering both fertilizer and protection against livestock providing better agriculture production. Abundances unused low quality land can reserve for the plant cultivation.

2.6 Biodiesel synthesis

2.6.1 Transesterification

The direct use of vegetable oil as engine fuel is impractical. This is because the oil has too high viscosity. High viscosity will lead to injectors cooking, carbon deposits and excessive engine wear (Fangrui, Milhord, 2000). In order to be used as diesel, the oil viscosity must to be reduced first. There are several methods to reduce vegetable oils viscosity. Dilution, micro emulsification, pyrolysis and transesterification are the four techniques can be applied to solve the viscosity problem (Dermibas, 2008), thereby improving the fuel atomization and consequently improve fuel combustion characteristics (S.Siller, 1997). However, the most common method used to reduce oil viscosity in biodiesel industry is by application of transesterification.

As defined by Dermibas (2008) in his book of "Biodiesel – A Realistic Fuel Alternative for Diesel Engines", transesterification which also called alcoholysis is the reaction of fat or oil triglyceride with an alcohol to form esters and glycerol. Figure 3.1 shows the chemical equation of transesterification reaction. A catalyst is usually present to improve the reaction rate and yield. Due to reversible process, methanol is used in excess to shift the equilibrium to product side.

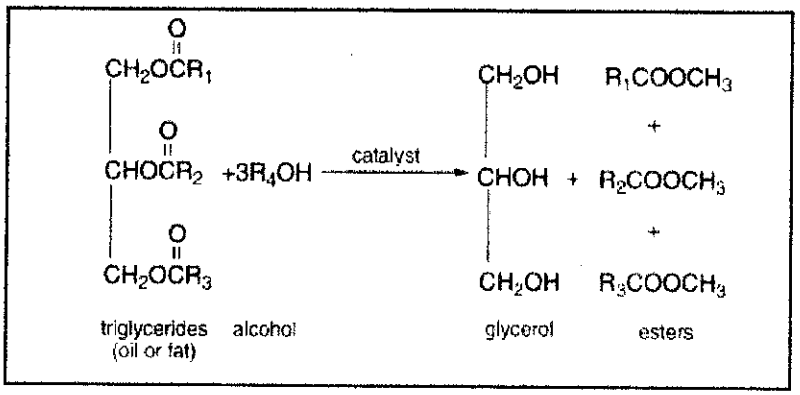


Figure 2.6: The general reaction for the transesterification of a triglyceride (Source: M. P. Dorado et al, 2004)

2.6.2 In-situ transesterification

According to K.G.Georgogianni (2007), conventional transesterification and in situ transesterification is differ in way that the kernel or the oil-bearing material of the seed is directly in contacts with acidified or alkalized alcohol in the transesterification process instead of reacting pre-extracted oil from the seeds with alcohol. The seeds will be macerated in alcohol during the process. The extraction and transesterification process on in situ is proceeding in one step, the alcohol acting both as an extraction solvent and an esterification reagent. By using this method, the quality of the seeds and the oil yield is not only being preserve, the seeds also are expected to produces more fatty acid methyl esters significantly greater compared to conventional transesterification by pre extracted oil (C. Stavarache, 2005). In addition to higher yield, the process and cost also is significantly reduced due to no pre-extracted oil process beforehand.

Research by S.Siler Marikonvic and A. Tomasevic (1997) has conclude the yield of methyl esters obtained from in-situ reaction were greater than those from conventional method. The research which has carried out by using sunflower oil as feedstock also study the composition of biodiesel product variation by in situ and conventional method, which the result has shown that the composition is unaffected using either method. However the cloud point of esters produced under in-situ method is found to be lower than conventional method.

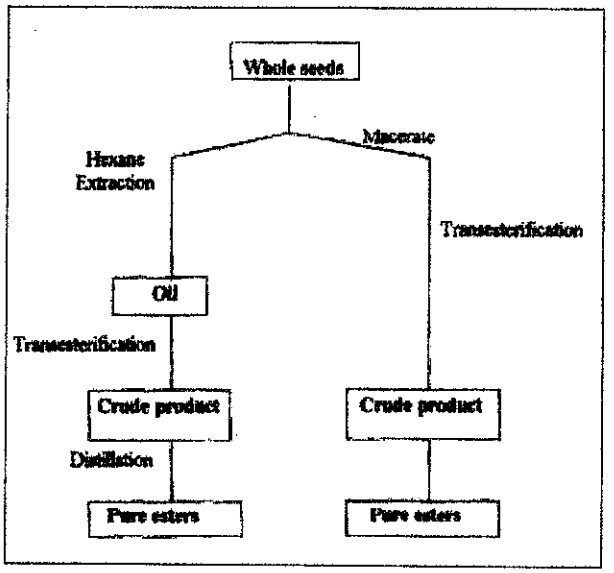


Figure 2.7: Conventional and in-situ transesterification process (S.Siller Marinkovich,1997)

2.6.3 Catalytic transesterification methods

Vegetables oils can be transesterified by heating it with anhydrous alcohol (methanol) in excess with the presence of a catalyst. The reaction can be catalyzed by alkalis, acids or enzymes. below are the general catalytic systems:-

a) Acid-catalyzed transesterification methods

Furuta et al (2003) had conducted the transesterification method using acid catalyst. The acid catalysts usually used are sulfuric acid, hydrochloric acid or sulfonic acid. The catalysts is dissolved into methanol by vigorous stirring in a small reactor which later on pumped into another reactor, followed by addition of oil bearing seeds for transesterification on in situ. The used of acid catalyst often neglected as the process is much slower compared to by using alkaline catalyst, however the used of acid catalyst ensure none saponification process occur. The fact that homogenous acid such as hydrochloric acid and sulfuric acid need longer time has encourage Furuta et al.(2003) to study the solid superacid as acid catalyst. The outcome of the research shows that the used of solid superacid catalyst such as tungstated zirconia alumina has positive result compared to sulfuric acid or hydrochloric acid.

b) Alkali catalytic transesterification methods

Jun Feng et al (2008) in their research, mix the cottonseeds (raw materials) into methanol-sodium hydroxide mixture. The mixture is then heated under reflux for 1–5 hour before proceed into further process. Zhang et al (2003) on the other hand use Potassium Hydroxide and Sodium Hydroxide as base catalyst. The catalyst is dissolved into methanol by vigorous stirring in small reactor and pumped into another reactor, followed by addition of oil bearing seeds for transesterification on in situ. The study of process design by Zhang et al has concluded the using of Alkali catalytic is simpler and faster with the least of equipment need for industrial means compared to acid catalyzed.

c) Enzymatic catalytic transesterification methods

The third method, enzymatic transesterification of triglycerides offer an environmentally more attractive option than the process discuss before. The method eliminated the need to remove the catalyst through neutralization or eventual separation from the ester which is hard to achieve. However the high cost of the enzymatic process makes the methods economically unattractive. Study by Noureddini et al. (2005) discuss the parameters need to optimize the process by immobilize the enzyme (Pseudomonas Cepacia) for recovery and reuse. The reaction yield as well as well as the reaction times is still unfavorable compared to base-catalyzed reaction systems (Schuchardt et al., 1998)

d) *Ion exchange resin methods*

Ion exchange might have greater potential to compare to enzymatic transesterification and supercritical alcohol in term of cost saving biodiesel production. The utilization of ion exchange study by Vicente et al. (1998) utilized ion-exchange resins for the transesterification of sunflower oil and methanol, but the conversion was less than 1% for each resin study. Up-till now, the successful transesterification with a high conversion and a high reaction rate using the ion-exchange resin has not been reported. The study is then continued by N.S.Kitakawa et al (2005), the study experimenting reaction of triolein with ethanol using various ion-exchange resin

catalysts to produce ethyl oleate as a biodiesel. The anion-exchange resins have found to exhibit much higher catalytic activities than the cation-exchange resin. Furthermore, The anion exchange resin with a lower cross-linking density and a smaller particle size gave a high reaction rate as well as a high conversion. By combining the three-step regeneration method, the resin could be repeatedly used for the batch transesterification without any loss in the catalytic activity. The reactor system of expand packet bed permitted the continuous production of ethyl oleate with a high conversion

2.6.4 Non- catalytic transesterification method

There are two non catalyzed transesterification processes:-

a) Biodiesel production with BIOX process

Develop originally by Professor David Boocock in 1999 this process uses a co-solvent such as tetrahydrofuran to solubilize the alcohol. Co-solvent options are designed to overcome slow reaction time cause by the extremely low solubility of the alcohol in the Triglyceride phase. Fast reaction (5 to 10 minutes) is achieved and no catalyst residues are found in either the ester or the glycerol phase. (Source: www.bioxcorp.com), Figure 3.2 shows BIOX cosolvent process

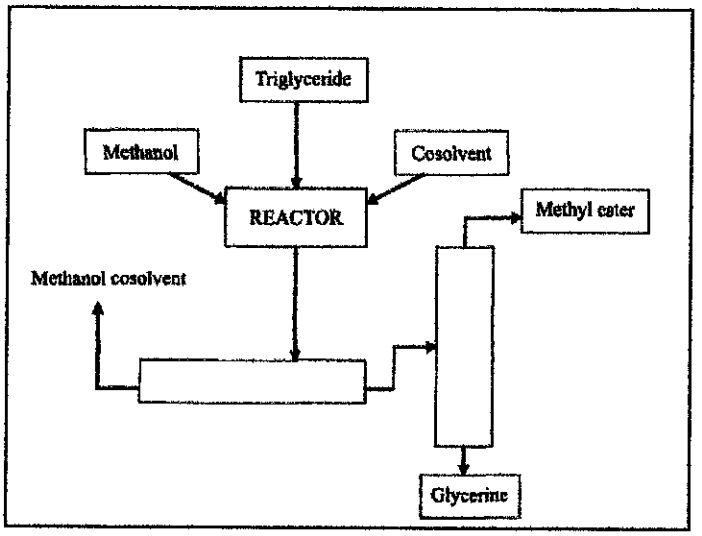


Figure 2.8: BIOX cosolvent process

b) Supercritical Alcohol Process

Supercritical methanol is introduced to solve the problems associated with the two-phase nature of normal methanol/oil mixtures by forming a single phase as a result of the lower value of the dielectric constant of methanol in the supercritical state. As a result, the reaction was found to be complete in a very short time (Han et al., 2005). In contrast to catalytic processes under barometric pressure, the supercritical methanol process is non-catalytic, involves much simpler purification of products, has a lower reaction time, more environmentally friendly, and requires lower energy use. However, the reaction requires temperatures of 525 to 675 K and pressures of 35 to 60 MPa (Demirbas, 2003, Kusdiana and Saka, 2004). Supercritical transesterification is carried out in a high-pressure reactor (autoclave). In a typical run, the autoclave is charged with a given amount of vegetable oil and liquid methanol with changed molar ratios. The autoclave is supplied with heat from an external heater, and power is adjusted to give an approximate heating time of 15min.. Transesterification occurs during the heating period. After each run, the gas is vented, and the autoclave is poured into a collecting vessel. The remaining contents are removed from the autoclave by washing with methanol. Figure 3.3 shows the supercritical transesterification method.

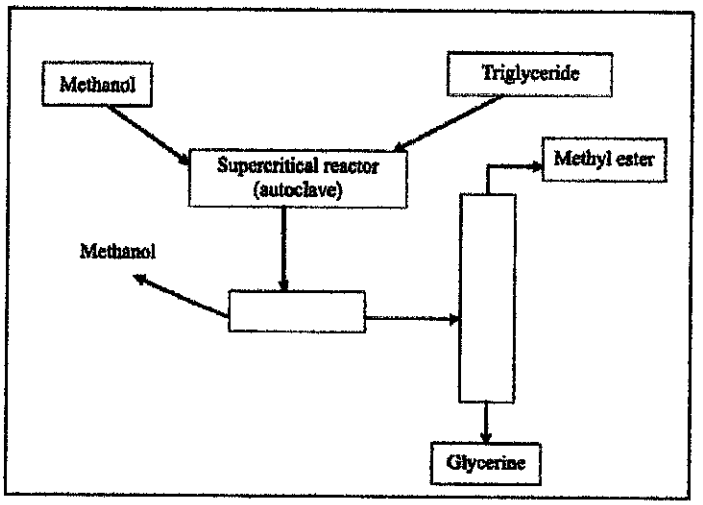


Figure 2.9: Supercritical transesterification process

c) Biodiesel production using ionic liquid process

An ionic liquid may be formed from a homogenous substance comprising one species of cation and one species of anion, or can be composed of more than one species of cation or anion. Earle, Martin and J.Martin et al (2005) have found that it is possible to produce biodiesel using an ionic liquid which is stable to reaction conditions, thereby allowing continued recycling. The acid or base functionality also can be incorporated into the ionic liquid to allow the ionic liquid to act as a catalyst or solvent.

2.7 Process intensification

Process intensification means improvement of a process, mainly the reaction by any possible means, to increase the overall productivity. This usually takes the form of reaction rate enhancement by extending known laboratory techniques to industrial scale production (Doraiswany.L.K, 2001).In organic synthesis, several techniques are known to give intensified effect of production. Among the techniques suitable for biodiesel productions are:

a) Sonochemistry (ultrasound)

Ultrasound energy is known to produce chemical and physical effects that arise from the collapse of cavitations bubbles. The collapse of cavitations bubbles disrupts the phase boundary in a two-phase liquid system and causes emulsification by ultrasonic jets that impinge one liquid in to the other .Researcher in Hielscher-Ultrasound Technology (1999) found that ultrasonication can achieve a biodiesel yield in excess of 99%. Ultrasound also reduces the processing time from the conventional 1 to 4 hours batch processing to less than 30 seconds. More importantly, ultrasonication reduces the separation time from 5 to 10 hours by using conventional agitation and mechanical stirring to less than 60 minutes. This technology does also help to decrease the amount of catalyst required by up to 50% due to the increased chemical activity. Other benefits are the amount of alcohol required can be reduced to about 15% in addition to higher purity of biodiesel obtainable.

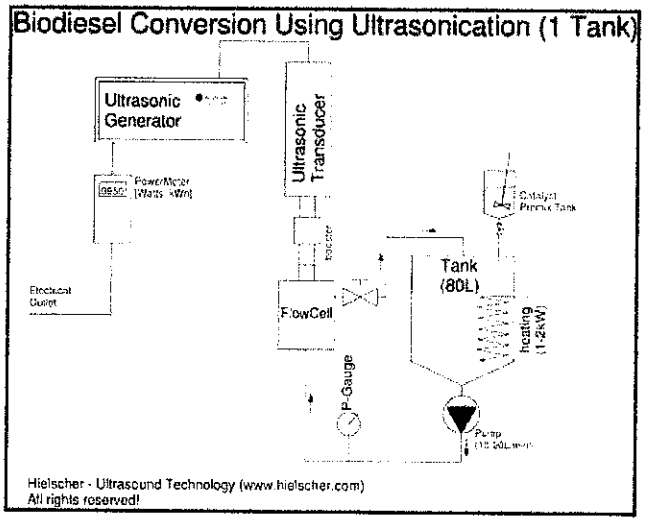


Figure 2.10: Biodiesel conversion using Ultrasonification Process flow diagram.

Study investigated by K.G. Georgogianni et al. (2007) also concluded that the use of ultrasonic cavitations increase the yield and rate of reaction significantly. The study which taking the concentration of Sodium Hydroxide, and the use of ultrasonication and mechanical agitation as variable, shows the best result is from the ultrasonication applied process.

b) Oscillatory flow reactor

Continuous reactor is more favorable than batch reactor due to the high quantity and quality of the product yield. Oscillatory flow in baffled tubes has been studied for many years and much work have been done in areas related to fluid dynamics, heat and mass transfer and residence time distribution. Many advantages have been characterized for oscillatory flow mixing, such as efficient dispersion for immiscible fluids, uniform particle suspension, gas-in-liquid dispersions and multiphase mixing (M.R Mackley et al., 1997).

Recent researches have indicated that oscillatory flow in a baffled tube has significant potential for process and product enhancement in a wide range of application. Continuous processing is achieved by superimposing an oscillatory flow on a steady throughput in a tubular reactor. Each inter-baffle zone is a unit stirred tank, and in a multi-pass configuration, a multiplicity of stirred tanks exists in series, allowing a close approach to plug flow RTD (Residence Time Distribution), even at low throughput rates. An operating advantage is that

residence time can be fixed, but control over RTD and heat transfer is maintained (Stonestreet and M.R Mackley, 1997).

In another study Stonestreet and Harvey reported that oscillatory flow reactor is a novel type of continuous reactor, in which tubes fitted with orifice plate baffles have an oscillatory motion superimposed upon the net flow of the process fluid. The interaction between the fluid and the baffles creates the oscillatory motion of vortex alike of the fluid that generates excellent mixing and enhanced transport rates in biodiesel production, whilst maintaining a close approach to plug flow. Oscillatory motion in the tube is provided by an electrically or pneumatically driven piston or diaphragm to oscillate the fluid or to displace series of baffled. Most Recent study by A.M Ghazali et al. 2008 conclude that oscillatory flow reactor give enhance process engineering properties such as mixing, heat transfer, homogeneous and heterogeneous phase mass transfer and most of all, the rate of reaction over plug flow reactor and the equivalent continuous reactor

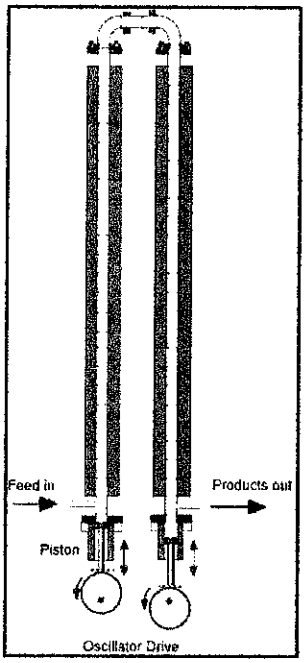


Figure 2.11: Oscillatory flow reactor schematic diagram

c) Heterogeneous catalyst

The use of heterogeneous catalyst could be an attractive solution to low operating cost. This is because the heterogeneous catalyst can be separated more easily from the biodiesel products compared to homogenous basic catalyst resulting in a higher quality esters and glycerol thus saving expensive refining expense. In 2006, a 160000 t/y commercial plant started up using heterogeneous catalyst. The plant which is based in Hesterflip-H technology used the heterogeneous catalyst mixed of oxide of zinc and aluminum. The plant manages to get glycerol purity level of 98%. (Source: Catalysis today, 2005).

The article wrote by Viswanathan and Ramaswamy (2007) describes the various types of heterogeneous solid acids and bases as promising catalysts for efficient biodiesel production via transesterification process. The catalysts are summarized in the table 1. Solid acid catalysts have the capacity to replace strong liquid acids, thereby eliminating the corrosion problems and the environmental waste pollutants. However, research dealing with the use of solid acid catalysts for biodiesel synthesis has been limited due to expectations of lower reaction rates and unfavorable side reactions. Thus the use of heterogeneous acid catalyst as catalyst in biodiesel production would not to be cover in the project study.

Table 1: Typical solid acid and base catalysts for transesterification

Solid Acid Catalyst	**Solid Basic Catalyst**
Sulphonic ion exchanged resin	Hydrotalcites (Mg-Al)
Amberlyst -15	Cs-exchanged sepiolite
Nafion	Oxides like MgO, CaO, La2O3, ZnO
Unstated Zironia-alumina	Quanidine anchored cellulose/polymer
Sulphated tin oxide	NN'N" tricyclohexyl quanidine
Sulphated zirconia/alumina	encapsulated in Y zeolite
Zeolites (H-Y) H-Beta, H-ZSM-5, ETS-4,10	Metal salts of amino acids
	CaCO3, Ba(OH)2
MCM family	Cs exchanged faujasites
Heteropoly acids	Li-promoted CaO
H3PW12O40, H4SiW12O40	KxX/Al2O3 (X- halide ion or other
Cs2.5H0.5PW12O40	mono/di-valent anion)
Zinc acetate on silica	Zinc aluminates
Organosulphonic acid on mesoporous silica	
Mesoporous unstated zirconium phosphate	

A.Kawashima et al, (2008) in their study investigate the uses of heterogeneous base catalysts for the transesterification of oil to aimed effective production of biodiesel. Thirteen different kinds of metal oxides containing calcium, barium, magnesium, or lanthanum were prepared as catalysts. Their catalytic activities were tested for transesterification at 60°C with a 6:1 molar ratio of methanol to oil and a reaction time of 10h. The calcium containing catalysts $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and $CaO\text{-}CeO_2$ showed high activities and approximately 90% yields of methyl ester. Furthermore, catalytic durability tests were performed by repeating the transesterification reaction several times with the calcium containing catalysts recovered from the previous reaction mixture. The catalyst with good durability is characterized as good catalyst selection. It was found that CaZrO3 and $CaO\text{-}CeO_2$ show high durability and have the potential to be used in biodiesel production processes as heterogeneous base catalysts

Other study by Gryglewicz (1999) has investigated the possibility of using alkaline-earth metal hydroxides, oxides, and alkoxides to catalyze the transesterification of rapeseed oil at methanol reflux temperature. He found that sodium hydroxide was the most active, barium hydroxide was slightly less active, and that calcium methoxide showed medium activity. The reaction rate was lowest when CaO powder was used as catalyst while magnesium oxide and calcium hydroxide showed no catalytic activity at all. CaO as a catalyst reactivity however increases with increase in the temperature and methanol/oil molar ratio.Leclercq et al. (2006) on the other hand tested the use MgO/Al2O3 hydrotalcites and MgO in the transesterification of rapeseed oil. They found that MgO was more active than hydrotalcites.

In this paper, study of the performances of different heterogeneous catalysts will be reported to evaluate the possibility of their use in the production of biodiesel using Jatropha seeds. The heterogeneous catalysts performances to be study will be CaZro3, $BaOH_2$, Ca(OCH3)2, $CaCO_3$ and MgO. The catalysts were selected based on previous studies review and availability of the catalysts in the chemical laboratory.

2.8 Analytical methods

Biodiesel produced need to go through series of analytical analysis to certify that the fuel produced meets its standard specification. Possible analysis techniques from analytical engineering handbook and as discussed by M.R Mackley (1997) in his presentation are:-

a) *Percentage yield*

The analysis technique is a quantitative analysis helpful to optimize the reaction or to study the parameters such as effect of the addition of different amounts of catalyst, or different temperatures of reaction. The theoretical products yield may be very challenging to determine. The simple yield calculation of how many grams is produced/gram of starting material can be used.

b) *Higher Heating value / Calorimetric*

This process can be done by burning a known amount of biodiesel produced in a crucible and using the released energy to heat a known amount of water to determine the amount of energy released.

c) *Thin layer chromatography*

TLC is a very common method to determine how many different compounds are present in a sample. This test provides qualitative information about how many different compounds are present in a mixture and allows determine if two different samples contain different materials. For this analysis technique, very small quantities of the samples will be placed on the special TLC plates. The plate is put in a container with a solvent or solvent mixture. The solvent runs up the plate and will separate the different kinds of molecules based on polarity differences and size differences.

d) Viscometry

Viscometry is the process of testing the viscosity of a substance. Vegetable based oils tend to be fairly viscous and don't flow too easily, which is bad for a fuel. Biodiesel with smaller molecules contents tends to flow relatively easily. Using viscometry one can compare the viscosity of different oils with the biodiesel produce. Other than helping to ensure the reaction did occur, the analysis also can be used to compare biodiesels from different oils.

e) Gas chromatography

The techniques allows for separation of mixture by its boiling point. The method is more effective than TLC methods.

f) Karl Fisher titration

Method that uses coulometric or volumetric titration to determine the trace amounts of water in sample. The biodiesel should be ensure free of water for best performance.

g) Flash point tester

Method to determine the lowest temperature at which vapors from a test portion combine with air to give a flammable mixture and 'flash' when an ignition source is applied. Flash point is measured by apparatus named "open cup" or "closed cup". "Open cup" tests are required in some specifications and regulations, and are intended to mimic conditions in open spaces whereas "closed cup" tests are closer to most situations, where space is restricted. "Closed cup" tests are more usually specified as the test results are less affected by laboratory conditions and give a more precise and safer result. There are 4 major "closed cup" flash point tests which are specified nationally and internationally for testing fuels and other materials.

2.9 Raw materials

2.9.1 General

Jatropha or the scientific name Jatropha Curcas L (JCL) is types of plant that usually grow on wasteland. JCL grows almost anywhere, will it be gravelly, sandy or saline soils. It can even thrive on the poorest stony soil and grow in the crevices of rocks (Wikipedia, 2007). Biodiesel technology based on Jatropha was developed in India initially. Now other Asia country such Philippines and Indonesia begin to give attention to plantation of Jatropha. In Malaysia, Jatropha plantation is still in unofficial small scale. However planning to produce high yield Jatropha clones and regulate large-scale Jatropha plantations on marginal land is on the move by The Malaysian Rubber Board.

The plant can yield more than four times as much fuel per hectare as soybean, and more than ten times compare to maize. In fact, a hectare of Jatropha can produce about 1,892 liters of fuel (Michael Fitzgerald, 2006)

The tree structure can be small or large shrub, with up to 5–7 m tall, with a soft wood and a life expectancy of up to 50 years. The plant develops a deep taproot and initially four shallow lateral roots. The taproot theoretically may stabilize the soil against landslides while the shallow roots are alleged to prevent and control soil erosion caused by wind or water, the potential however has not been investigated scientifically yet. The blackish seeds of most provenances contain toxins, to such levels that the seeds, oil and seed cake are not edible without detoxification (Becker et al. 1997).

JCL's high ecological adaptability allows it to grow in a wide range of conditions. As a succulent that sheds its leaves during the dry season, JCL is well adapted to semi-arid conditions, although more humid environmental conditions are shown to result in better crop performance. According to Heller J (1996), JCL can tolerate extremes high-temperature extremes, but not frost condition, as it may causes immediate damage. Thus the plant is not suitable to be plant on four seasonal countries. JCL can grow in a wide range of soils. Well-drained sandy or gravelly soils with good aeration are preferred.

Figure 2.12: Jatropha plant and the ripe seeds

The JCL oil contains more than 75% unsaturated fatty acid, which is reflected in the pour and cloud point of the oil. The fatty acid composition of JCL oil is dominated by oleic acid and linoleic acid. The maturity stage of the fruits at the moment of collection is reported to influence the fatty acid composition of the oil (Raina AK, Gaikwad BR, 1987). Figure 5.2 and 5.3 shows the composition, characteristics of oil in JCL and the percentage of fatty acid composition respectively. The composition and characteristics of oil heavily depend on the cultivation quality and genetic from surrounding.

Table 2: JCL oil composition and characteristics (Sources: W.M.J Achten, 2007)

	Range	Mean	S.D.	n
Specific gravity (g cm $^{-3}$)	0.860–0.933	0.914	0.018	13
Calorific value (MJ kg $^{-1}$)	37.83–42.05	39.63	1.52	9
Pour point (°C)	−3			2
Cloud point (°C)	2			1
Flash point (°C)	210–240	235	11	7
Cetane value	38.0–51.0	46.3	6.2	4
Saponification number (mg g $^{-1}$)	102.9–209.0	182.8	34.3	8
Viscosity at 30 °C (cSt)	37.00–54.80	46.82	7.24	7
Free fatty acids % (kg kg $^{-1}$*100)	0.18–3.40	2.18	1.46	4
Unsaponifiable % (kg kg $^{-1}$*100)	0.79–3.80	2.03	1.57	5
Iodine number (mg iodine g $^{-1}$)	92–112	101	7	8
Acid number (mg KOH g $^{-1}$)	0.92–5.16	3.71	2.17	4
Monoglycerides % (kg kg $^{-1}$*100)	nd–1.7			1
Diglycerides % (kg kg $^{-1}$*100)	2.50–2.70			2
Triglycerides % (kg kg $^{-1}$*100)	88.20–97.30			2
Carbon residue % (kg kg $^{-1}$*100)	0.07–0.64	0.38	0.29	3
Sulfur content % (kg kg $^{-1}$*100)	0–0.13			2

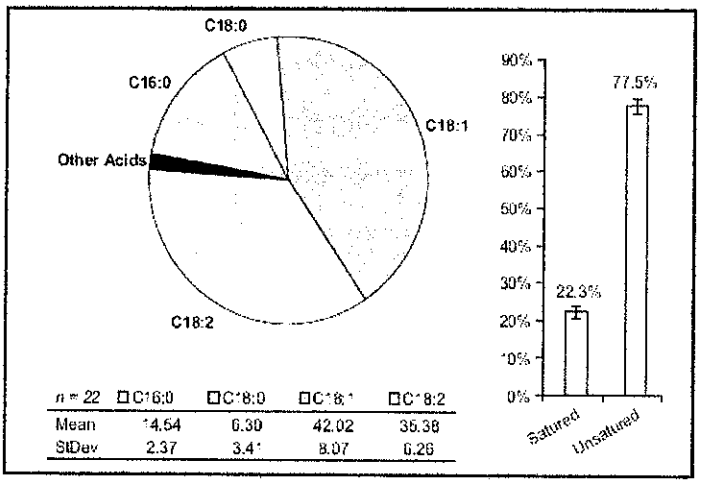


Figure 2.13: Fatty acid composition percentage (Sources: W.M.J Achten, 2007)

2.9.2 Jatropha biomass (seed cakes)

The seedcake of Jatropha which consists of crushed shell and kernel also has its own use. For every 3 tons of Jatropha seeds, 1 tons yield the crude oil while the other 2 tons yield the biomass (seedcake). After go through the oil extraction process in conventional method using screw press machine, the seedcake still has about 5 to 7 percent of residual oil. This property qualified the seedcakes to be a good combustible material with caloric value approximate to 22MJ/Kg. Laboratory test conducted by ITS testing services (2006) has reported the calorific value of seed shell and seedcake to be 19.5MJ/Kg and 22MJ/Kg respectively. The value is almost similar to low grade coal calorific value, with the value of 22 -27MJ/Kg for average coal.

Other usages of Jatropha biomass also include biomass briquetting, organic fertilizer and animal feed. Biomass briquetting is used for micro gasification generating electricity and for steam generation in power plants. The biomass which is also rich with Nitrogen Phosphorus Potassium (NPK) is a good organic fertilizer. The product can be utilized by reusing it in Jatropha plantation or sell as organic fertilizer for general use. The animal feed possibility is however still under study due to its toxic properties. The biomass which containing 24% of protein need to go through further large scale economical detoxification study before it's become reality. (Source: Jasmine Yong, Jatropha biomass for rural development, 2007)

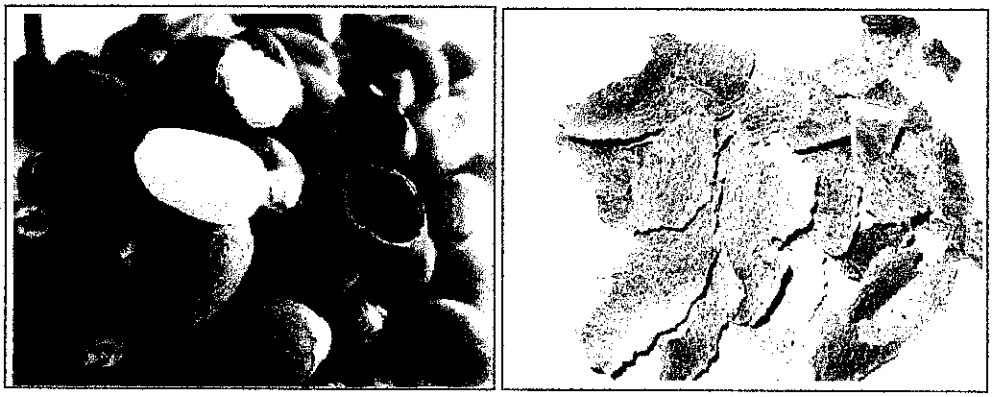


Figure 2.14: Jatropha seed shell and seed cakes.

2.9.3 Jatropha in medical

Study by Xu Ying and Chen Fang (2007) has highlighted the potential of Jatropha as medicine. This high tolerant to pathogen plant was study to has medical therapeutic activities. The water extracted from the branches of Jatropha tree inhibited strongly the HIV- induced cytopathic effects with low cytotoxicity. Cytopathic effects which refer to degenerative changes in cell showed the anti-virus activity properties of the plant. The plant also has anti-tumor activity properties. This is showed by chloroform extract which extracted from Jatropha roots that inhibit 79.5% of stomach tumor. Other study also found that the plant has anti fungi therapeutic activity which is showed by the inhibition of the plant to B. haptosporus and B.ranarum from fungi family. The source of the medical value from Jatropha comes from its Ribosome-inactivating proteins (RIPs). There is two type of RIPs, type 1 only having A chain and type 2 having A and B chain. Type A RIPs is the one in Jatropha which what give the plant its toxicity properties. However, the toxicity of curcin in type A is only 1 per 300000 of ricin in type 2 B chains RIPs. (Source: Xu Ying, Chen Fang, the Application of Bioactive Compounds from *Jatropha* as Medicine)

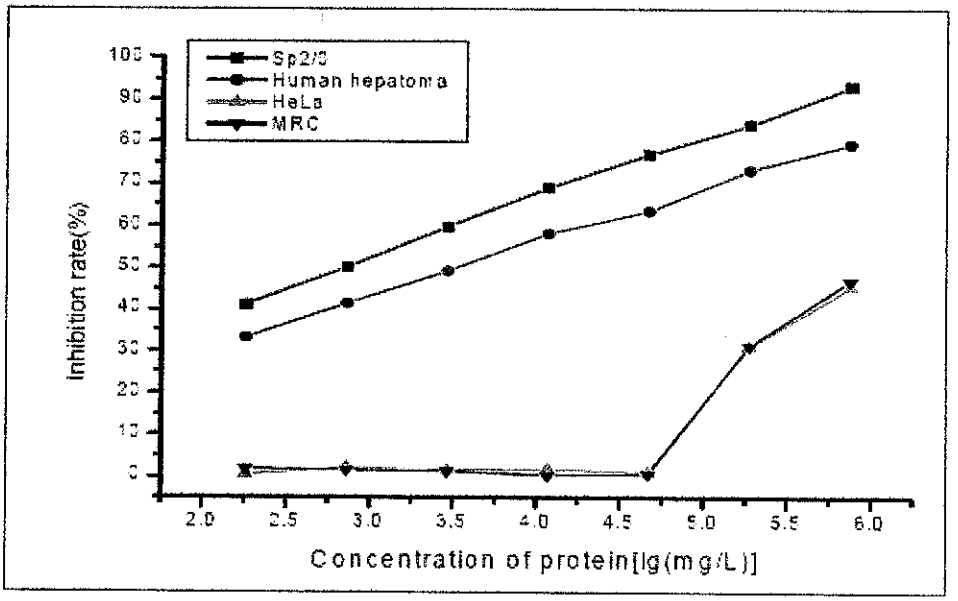


Figure 2.15 Anti-tumor activity: The inhibition graph of curcin on Human hepatoma, Sp2/0, HeLa and MRC

2.10 Recent research work in UTP

The chapter will discuss on the outcome of recent research project in UTP which related to the researcher project.

The first research project is from Iskandar bin Zakaria (2008) entitled the effect of ultrasonic water bath on in-situ transesterification of Jatropha seed. Iskandar aims to investigate the most optimal condition of in situ transesterification process to achieve the most maximum biodiesel production. The parameters studies by Zakaria are:

i. Catalyst and catalyst strength

ii. Temperature

iii. Mixing intensity (RPM)

The experiment is carried out conventionally by using mechanical stirring with Sodium hydroxide and potassium as basic catalyst to find the optimum condition prior proceeding with ultrasonic application. The results of the project conclude the longer extraction time is not necessary and 2 hours of extraction sufficient for 50% oil yield. The highest oil yield percentage in one time also can be achieved by increasing the catalyst concentration. For homogenous catalyst performance, Sodium hydroxide at 1.5wt% show better performances compared to Potassium hydroxide. Temperature at 60°c and mixing intensity 500RPM is also selected as the best optimum condition to be use in conventional method. Another experiment to study the ultrasonic power as manipulating variable has concluded the use of 120% to give the highest oil yield compared to 60% and 80%.

Another research project from Widya (2006) studied on the transesterification of rubber seed. She has investigated the effect of several parameters such as the effect of alcohol used, the type of homogenous catalyst, the alcohol to oil molar ratio and the catalyst strengths effects. The outcome of the project concluded the use of ethanol as the best alcohol solvent compared to methanol in first stage esterification process. The use of Acid sulfuric as homogenous catalyst has shown high yield of product but low in reaction rate. The second step of experiment of base transesterification however had shown the use of methanol giving higher yield than ethanol.

Thus methanol will be used in Jatropha one stage transesterification process. The methanol however has advantage over ethanol for its cheaper prices. Between Potassium and Sodium Hydroxide, the use of 1%wt Sodium hydroxide is studied to gives better performance. The relevance finding from the project will be applied alongside the international literatures findings in author research project.

CHAPTER 3: METHODOLOGY AND PROJECT WORK

The chapter will discuss on the experimental methodologies and any other procedures related. Brief information on project work plans and the flow is included in the following table.

Table 6: Experiment Planning and flow

Section	Sub-section	Description
Preparation	Jatropha seeds acquisition	To perform acquisition of the raw material whether from available sources or fresh picked.
	Extraction of oil from Jatropha seed using Soxhlet/Hexane Extractor	To analyze the amount of oil extracted from rubber seed using hexane as solvent.
	Acid Base Titration	To perform acid-base titration to identify the free fatty acids (FFA) contents in the vegetable oils.
Experimental	In-situ transesterification in ultrasonic bath.	To conduct in-situ transesterification of Jatropha in various parameters: i. Effect of catalyst ($CaZrO_3$, $Ba(OH)_2$, MgO, $CaCO_3$, $Ca(OH)_3$) 5.0%, 60°c ii. Effect of catalyst strength (3%, 5%, 7%). iii. Effect of ultrasonic power (40%, 80%, 120%) iv. Effect of alcohol ratio w/v (1:4, 1:5.5, 1:7) v. Effect of alcohol type vi. Effect of raw materials and catalyst reusability vii. Transesterification using oil
Analytical Testing	Thin Layer Chromatography (TLC)	To qualitatively determine the type and components present (existence of biodiesel).

3.1 Chemicals

The chemicals used throughout the project are:

Table 7: Chemicals used for laboratory works

Section	Chemicals	Quantity
Preparation	Hexane (95%), Fischer Scientific (Analytical Reagent Grade)	1.0L
	Phenolphthalein ,Merck, (Powders)	0.1L
	Isopropyl Alcohol, Merck (Pro Analysi)	0.5L
	NaOH (Pellet), R&M Chemicals	10g
Experimental & Analytical	$CaZrO_3$ 99.7%, Aldrich	50g
	$Ba(OH)_2$, Syterm (ChemAR)	50g
	$CaCO_3$, Systerm (GPR)	50g
	MgO, Fischer Scientific (Laboratory Reagent Grade)	50g
	$Ca(OCH_3)_2$, 97%, Aldrich	20g
	Methanol, Merck (Pro Analysi)	3.0L
	Ethanol, Merck (Pro Analysi)	500ml
	Petroleum ether, Fischer Scientific Analytical Reagent Grade	0.5L
	Diethyl Ether, Fischer Scientific Analytical Reagent Grade	0.07L
	Acetic acid glacial, Systerm, ChemAR	0.01L
	Iodine Crystal, Gene Chemical	1
	Chloroform, R&M Chemicals	

3.2 Apparatus and Equipment

The equipment and apparatus used for experiments are:-

Table 8: Apparatus / Equipments for laboratory works

Section	Apparatus/ Equipment
General use	Beaker, Graduated cylinder, Round bottom flask, Conical Flask
Preparation	Heating Oven, Grinder, Soxhlet Extractor, Thimbles, Reflux condenser, Retort stand, Weighing scales (Mettler Toledo), Heating mantle
Experimental	Ultrasonic water bath 10% to 140% power (Transsonic Digital), Buchnell filtration unit, Separation funnel, rotary evaporator equipment (Buchi), Silica plates (Whatman), TLC chamber, (Camag), Capillary tubes

3.3 Experimental procedures

3.3.1 Preparation

3.3.1.1 Jatropha seeds preparation

Objective:

To prepare the seeds to be used in the experiment

Methodology:

Two sources of seeds were used in the experiment. One from previous researcher (6 months improper storage) and the other one is fresh ripped seeds, for the latter, the seeds were bought from a nursery in Malacca in the form of fresh seeds. Upon received, the seed is stored in a container containing silica sorbents to preserve the quality of the seeds. The seeds were then dried under the sun light to remove the moisture contents. After some time, the seeds outer were de-hulled, ground and stored in an air tight container.

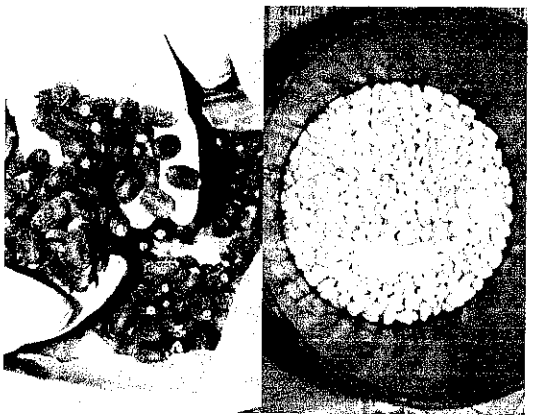


Figure 3.1: a) Jatropha seeds, b) De-hulled Jatropha seeds

3.3.1.2 Extraction of Jatropha seed using Soxhlet Extractor

Objective:

To determine and verify the amount of oil yield from conventional vegetable oil extraction using specific solvent

Methodology:

The experiment is carried out inside the fume hood. 20 gram of Jatropha seeds were weighed and filled into a thimble. The thimble was placed into a Soxhlet container which was connected onto round bottom flask containing 140ml (Surya, 2007) of Fisher Scientifics' analytical grade Hexane .Solvent in the round bottom flask is heated to boiling by using a heating bed. As the hexane vaporizes and rises into the Soxhlet container, it seeps through the permeable cellulose thimble and thus extracting oil from the samples put in the thimble. Extraction process is considered complete when the color of the liquid in the Soxhlet container similar to the color of liquid in round bottom flask. Purification was carried out by rotary evaporator to separate vegetable oil from the Hexane. The percentage of oil yielded can be calculated by using equation 3.1.

$$Oil\ yield\ (\%) = \frac{Oil\ weight}{Sample\ weight} \times 100\% \qquad 3.1$$

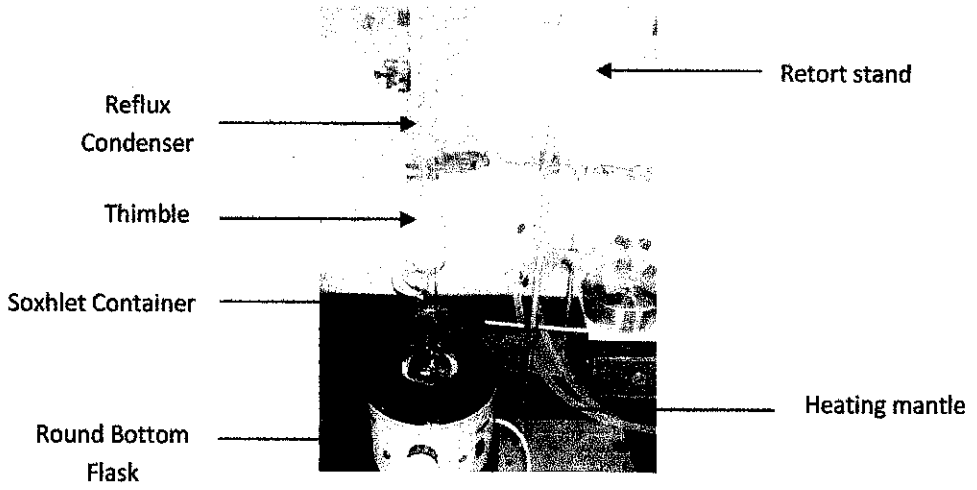


Figure 3.2: Soxhlet Extractor unit

3.3.1.3 Acid value measurement titration

Objective:

To determine acid value or verify the free fatty acid percentage of Jatropha seeds

Methodology:

50 ml Merck's Pro Analysi isopropyl alcohol was added into 250ml conical flask followed by 2 to 3 drops of phenolphthalein. The solution is titrated with NaOH until the solution color change from colorless to purple color. Any weight of oil (weight of 1ml oil was used in the experiment) extracted in previous experiment was then added into the solution. At this state, the solution's color return to initial colorless color. The solution is then titrated with NaOH until the solution color once again turn to purple color. The end reading is taking as endpoint. To calculate the acid value and percentage of free fatty acid, equation 3.2 and 3.3 were used.

$$FFA\% = \frac{(A - B) \times 25.6 \times N}{M} \qquad 3.2$$

$$Acid\,Value = \frac{(A - B) \times 56.1 \times N}{M} \qquad 3.3$$

A = Final burette reading N = Concentration of NaOH (N)

B = Initial burette reading M = Weight of oil (g)

3.3.1.4 Catalyst preparation

The catalysts used are from several suppliers. None of it were self–synthesizes. The catalysts in the form of powders were prepared according to the amount of oil extracted from Soxhlet extraction experiment. The calculation is as following.

$$Amount\ of\ catalyst\ = Desired\ catalyst\ strength\ (\%)\ \times\ weight\ of\ oil\ extracted \quad 3.4$$

The catalyst strength is decided by researcher parameters and the weight oil extracted is referred from the weight of oil extracted in experiment.

3.3.2 Experimental

3.3.2.1 In-situ transesterification using ultrasound water bath (Effect of Catalysts)

Objective:

To determine which type of heterogeneous catalysts giving the best performance together with application of heterogeneous catalyst, ultrasonic and in-situ transesterification application

Methodology:

5 types of 5% heterogeneous catalyst ($NaZrO_3$, $Ba(OH)_2$, MgO, $CaCO_3$ and $Ca(OCH_3)_2$ were selected for these experiment based on the literature review from previous chapter. The solution is prepared by adding each catalyst powder into separated conical flask containing 7:1 Methanol to oil w/v ratio and were let in ultrasonic water bath for 5 minutes at 60°c temperature, 80% ultrasonic power before add in 10 gram of ground Jatropha seeds to promote initial mixing. The experiment was carried 3 times (30 min, 60 hour and 90 hour). The products were filtered using Buchnel filter with vacuum filtration unit to separate catalyst and the seeds from the mixture, followed by purification using the rotary evaporator to separate the alcohol from the oil. TLC analysis and oil yield calculations were conducted for data analysis. The oil yield percentage was calculated using equation 3.5.

$$Oil\ yield\ (\%) = \frac{Oil\ weight}{Approximate\ oil\ contents\ weight\ in\ sample} \times 100\% \quad 3.5$$

3.3.2.2 In-situ transesterification using ultrasound water bath (Effect of Catalyst strength)

Objective:

To determine the heterogeneous catalysts strength giving the best performance together with application of heterogeneous catalyst, ultrasonic and in-situ transesterification application

Methodology:

The best 3 type of catalysts were selected from previous experiment. The solution is prepared by adding the catalyst with different catalyst strength (3% and 7%) into separated conical flask containing 7:1 Methanol to oil w/v ratio and were let in ultrasonic water bath for 5 minutes at 60°c temperature, 80% ultrasonic power before add in 10 gram of ground Jatropha seeds.. The experiment was carried 3 times (30 min, 60 min and 90 min). The products were filtered using Buchnel filter with vacuum filtration unit to separate catalyst and the seeds from the mixture, followed by purification using the rotary evaporator to separate the alcohol from the oil. TLC analysis and oil yield calculation were conducted for data analysis.

3.3.2.3 In-situ transesterification using ultrasound water bath (Effect of Ultrasonic Power)

Objective:

To study the effects of ultrasonic power together with application of heterogeneous catalyst, ultrasonic and in-situ transesterification application

Methodology:

By using the best parameters from previous experiment, the solution is prepared by adding the catalyst at 5% strength into separated conical flask containing 7:1 Methanol to oil ratio and were let in ultrasonic water bath for 5 minutes at 60°c temperature before add in 10 gram of ground Jatropha seeds. The experiment was carried for 60 minutes using 2 ultrasonic power variables (40%, and 120%). The products were filtered using Buchnel filter with vacuum filtration unit to separate catalyst and the seeds from the mixture, followed by purification using the rotary evaporator to separate the alcohol from the oil. TLC analysis and oil yield calculation were conducted for data analysis.

3.3.2.4 In-situ transesterification using ultrasound water bath (Effect of Alcohol/Oil v/w ratio)

Objective:

To study the effects of alcohol to oil v/w or molar ratio variation together with application of heterogeneous catalyst, ultrasonic and in-situ transesterification application

Methodology:

The procedures are almost similar to previous experiment. Using the best parameters from previous experiments, the in-situ transesterification were conducted with variation of methanol to oil w/v% ratio. The effect of 1:4, 1:5.5 and 1:7, Methanol to oil ratio were studied and carried for 60 minutes. TLC analysis and oil yield calculation were conducted for data analysis.

$$\frac{\rho \ of \ alcohol \times Volume \ of \ alcohol}{MW \ of \ alcohol} \times \frac{MW \ of \ oil}{Mass \ of \ oil} \qquad 3.6$$

3.3.2.5 In-situ transesterification using ultrasound water bath (Effect of Alcohol type)

Objective:

To study the effects of alcohol type together with application of heterogeneous catalyst, ultrasonic and in-situ transesterification application

Methodology:

The procedures are almost similar to previous experiment. Using the best parameters from previous experiments, the in-situ transesterification were conducted by replacing methanol with ethanol for 60 minutes. TLC analysis and oil yield calculation were conducted for data analysis

3.3.2.6 In-situ transesterification using ultrasound water bath (Catalyst reusability)

Objective:

To study reusability of the raw materials and the catalyst

Methodology:

The procedures are almost similar to previous experiment. The in-situ transesterification were conducted by using 50 gram of Jatropha seeds mix with $Ca(OCH_3)_2$ 5% in 1:4 w/v% methanol for 60 minutes at 120% ultrasonic power. The products were filtered using Buchnel Filter and re-used for second run (only alcohol is refilled). TLC analysis and oil yield calculation were conducted for data analysis

3.3.2.7 Transesterification using ultrasound water bath

Objective:

To apply the best parameter from previous experiment with transesterification process using extracted Jatropha seeds oil for comparison.

Methodology:

The procedures are almost similar to previous experiment. Using the best parameters from previous experiments, the transesterification were conducted by using 10 gram of Jatropha oil. The process runs for 60 minutes. TLC analysis and oil yield calculation were conducted for data analysis

3.3.3 Analytical

3.3.3.1 Thin Layer Chromatography

Objective:

To analyze the composition of product and the conversion of biodiesel from the experiment

Methodology:

A straight line is draw perpendicular 1 cm from the bottom side as the starting reference point. A solvent made of petroleum ether, diethyl ether and acetic acid glacial with volumetric ratio of 85:13.5:1.5 (vol %) or Hexane-Chloroform mixture with volumetric ratio 1:1 is prepared for plate development (Whichever solvent give clear images were used). 20 mL of the solvent is placed into a TLC chamber. The plate is then inserted into the chamber to be soaked. Due to capillary action, the solvent will rise and reached the 12 cm reference point. This process took about 20-30 minutes. The silica is then taken out and left to dry. A 10μL transferpette is used to extract the sample oil and is dropped on the starting point of the pre-soaked plate. The plate was again to be soaked-up till the final reference point. After plate development has completed, the plate is taken out and left to dry. The plate was then transferred into the iodine chamber containing iodine crystal to visualize the pattern developed on the plate. A clear image can be obtained when the plate is allowed to rest in the chamber for 24 hours. Image of the pattern is taken with a digital camera and to be analyzed. Each component in the sample was represented by the retention time. Different component traveled on the plate with different distance. Figure 3.2 can be use as references to blobs identification.

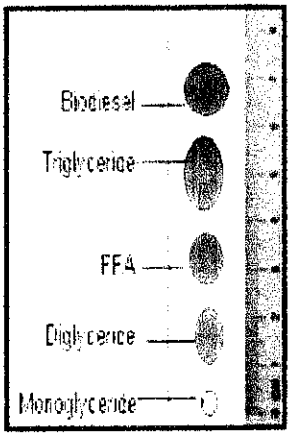


Figure 3.3: Detection of Product's Component on TLC Plates

Table 9: Detection Length of Different Component

Component	Detection Length (cm)
Biodiesel	5.00 – 7.00
Triglyceride (TG)	2.80 – 5.00
Free Fatty Acids (FFA)	2.30 – 3.30
Diglyceride (DG)	1.00 – 2.30
Monoglyceride (MG)	0.00 – 0.09

CHAPTER 4: RESULT & DISCUSSION

4.1 Extraction of Jatropha seed using Soxhlet Extractor

Initially, the experiment was carried out using the 5 months old raw materials (Jatropha) from previous graduated student research (will be called as old Jatropha seeds hereafter). Due to some problems, the experiment was repeated at later time using fresh bought Jatropha seeds. The extractions were carried out several times to take the average value of oil extracted. The time for extraction time was not study as previous study from Iskandar (2007) shown that the oil extracted independent of the extraction time taken. Moreover, the objective of the experiment only to find the amount of oil extracted data to be carried on for later experiment. Table 4.1 summarizes the outcome of the experiment.

Table 10: Jatropha oil yielded.

No	Raw materials (20 gram)	Weight of oil extracted (gram)	Oil yield (%)	Average of oil yield (%)
1	Old Jatropha seeds	2.50	12.5%	13.75
2	Old Jatropha seeds	3.00	15%	
3	New Jatropha seeds	8.00	80%	83.00
4	New Jatropha seeds	8.30	83%	
5	New Jatropha seeds	8.85	85%	

As seen on table 4.1, old Jatropha seeds shown very poor oil yield compared to fresh Jatropha seeds. This is due to improper storage practices of the seeds. The seeds which initially stored in heating chamber to reduced moistures degraded rapidly resultant from high fluctuating temperatures setting, ventilation of air and moisture. Although at standard condition storage, the oil contents would not affected up to 6 month (Jatrophabiodiesel.org). For new Jatropha seeds, the oil yield is very good compared to old Jatropha seeds. It is safe to conclude, the oil yield of Jatropha can be ranging from 50% (Iskandar, 2007) to 85%.

4.2 Acid value measurement titration

In conventional biodiesel synthesis, this experiment is crucial to determine the amount of heterogeneous alkaline catalyst (NaOH) to be use in transesterification. For this project, this experiment is aim to verify the free fatty acid (FFA) percentage in the vegetable oil. By knowing the percentages, one can determine whether to go for acid esterification first or directly to alkaline transesterification process. Table 4.2 included the free fatty acid contents percentage for oil extracted in previous experiment.

Table 11: Extracted oil FFA and acid value

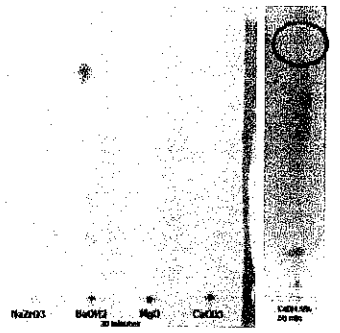
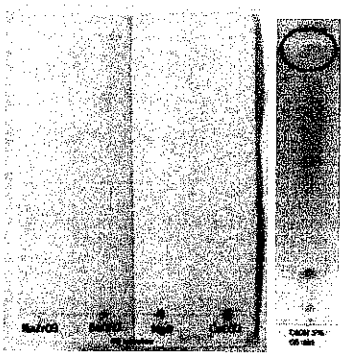
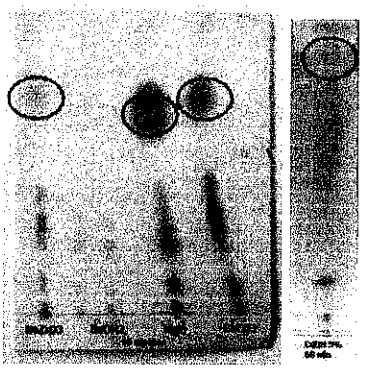
No	Raw materials (20 gram)	Titrated (ml)	Oil yield (%)	FFA (%)	Acid value
1	Old Jatropha seeds	12	12.5%	3.072	6.732
2	Old Jatropha seeds	14	15%	2.987	6.545
3	New Jatropha seeds	3.1	80%	0.248	0.543
4	New Jatropha seeds	2.5	83%	0.193	0.422
5	New Jatropha seeds	2.7	85%	0.195	0.429

It was found that the different between percentage of FFA in old Jatropha seeds and new Jatropha seeds are very high. This is because of poor storage as discussed earlier. Some also report, FFA percentage up to 4 percent is tolerable (WMRC Report). But to further process the oil from old Jatropha seeds are not efficient, due to its low yield of oil. New Jatropha seeds likewise, as expected, having very low free fatty acid percentages and high oil yield percentages. In this experiment, Jatropha claim to having low fatty acids is verified and can be undergo transesterification process directly. This study is significant in showing the important of using fresh raw material as biodiesel feedstock.

4.3 In-situ transesterification using ultrasound water bath (Effect of catalysts types)

The experiment aims to study the effect of different type of catalyst give the result as in table 4.3.

Table 12: Oil yield and observation for different catalyst

Time	Catalyst	Oil Yield (%w/w)	TLC observation
30 min (Run 1)	CaZrO3	31.2	
	$Ba(OH)_2$	29.0	
	MgO	18.62	
	$CaCO_3$	21.56	
	$Ca(OCH_3)_2$	19.13	
60 min (Run 2)	CaZrO3	51.13	
	$Ba(OH)_2$	25.75	
	MgO	14.55	
	$CaCO_3$	13.07	
	$Ca(OCH_3)_2$	36.13	
90 min (Run 3)	$CaZrO_3$	16.87	
	$Ba(OH)_2$	30.45	
	MgO	14.13	
	$CaCO_3$	15.15	
	$Ca(OCH_3)_2$	36.63	

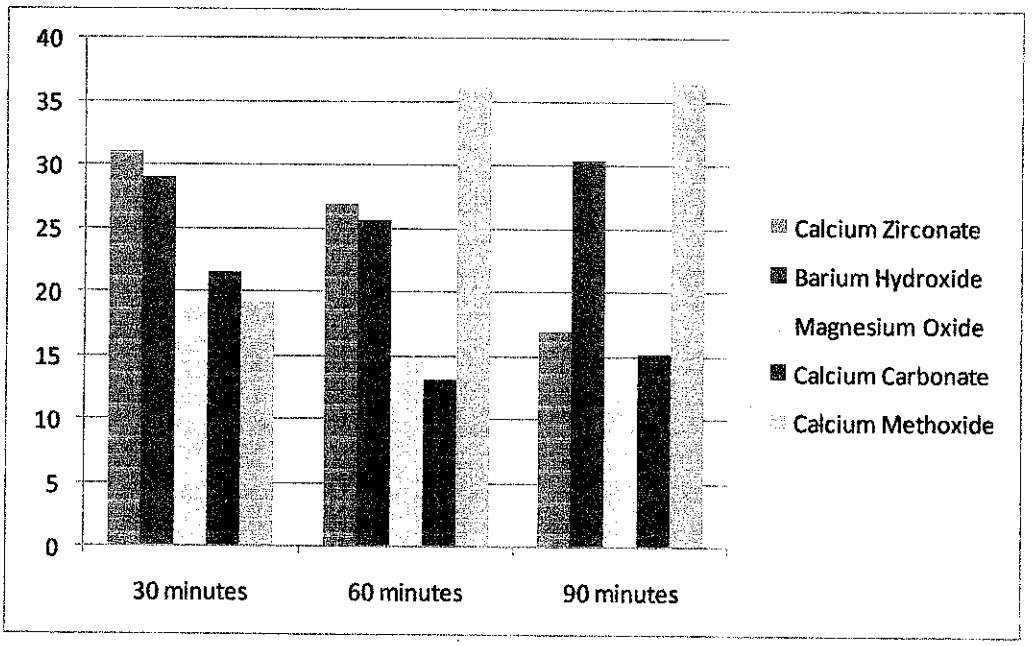


Figure 4.1: Oil Yield (%) versus time for different catalysts

In this experiment, temperature and ultrasonic power were kept constant at 60°c (Iskandar, 2008) and 80% (Fathin, 2008) respectively and types of catalyst were set as variable at 30 to 90 minutes time study. From TLC analysis observation at table 4.3, we can see that biodiesel formed only by using $Ca(OCH_3)_2$ as catalyst at 30 minutes and 60 minutes. The percentage of oil yielded also considered good at 60 minutes and 90 minutes. Nevertheless, for other type of catalyst, there were biodiesel formed at 90 minutes time study. $CaZrO_3$, MgO, $CaCO_3$, and $Ca(OCH_3)_2$ shown catalytic activity with MgO giving the highest proportions of biodiesel yield. Although samples using $Ba(OH)_2$ as catalyst shown greater oil yielded compare to others, the used of this catalyst would not benefit the production of biodiesel. This clearly contradicted with Gryglewiz (1999) and Wiswanathan (2006) finding. A possible explanation is the studies conducted previously are using conventional method, where the oil is pre-extracted. In in-situ, the catalyst reacting with methanol before the oil is actually extracted, giving product that yield more oils, but not biodiesel conversion. Wiswanathan also lining this catalyst to be having some homogenous properties, this also explain why the oil yield looks higher than other, while in fact there is water contents in the oil. Soluble barium compounds are highly toxic, thus this type of catalyst is dropped from further study. $Ca(OCH_3)_2$ and MgO is selected to be used for the next experiment.

4.4 In-situ transesterification using ultrasound water bath (Effect of catalysts strengths)

In the experiment, the temperature and ultrasonic power were kept constant as previous experiment. The catalyst strength as manipulated variable is set at 3% and 7%. This experiment aimed to study the relationship of catalyst activity to catalyst strengths at the same time to find whether higher catalyst strengths are necessary for biodiesel production or adequate by only using low catalyst strengths. The first trial of experiment at time study 60 min and 90 min were not successful as the oil yield was very small. It is about less than 5% and it is hardly able to remove it from the rotary evaporator flask for collection. The experiment which initially used $CaZrO_3$ and MgO as catalysts giving emulsified oil as end product. The emulsified oil or wax gel products are resulted of very low cloud point. The factor contribute to low cloud point is the existence of minor components such as mono-glyceride and di-glyceride as the result of incomplete reaction (Pfalzgraf, 2007). Higher catalyst strengths also might cause catalyst poisoning, hindering the reaction of the glycerides into biodiesel, decreasing the catalyst strength might help reducing cloud point problem, but at the cost of oil yield and biodiesel conversion.

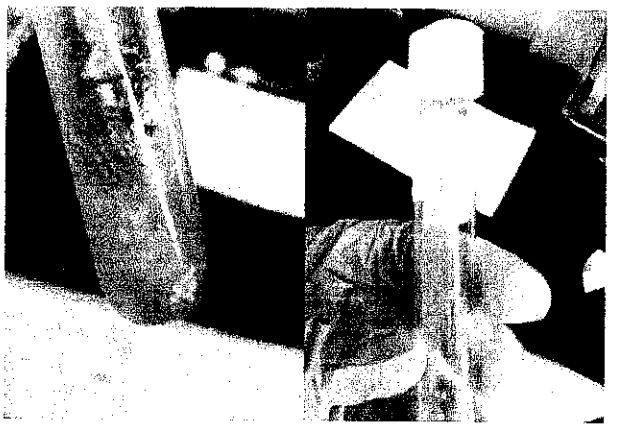
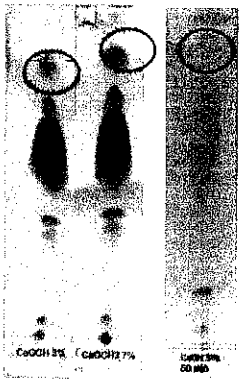
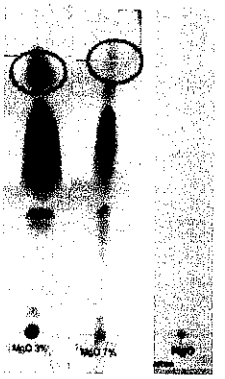


Figure 4.2: Gel/Emulsified oil product

Second attempt of similar experiment was done using MgO and $CaO(CH)_3$ as catalyst at later time . The result is as table 4.4 and figure 4.2.

Table 13: Oil yield and observation for $Ca(OCH3)_2$ and MgO at different catalyst strengths

Catalyst	Catalyst Strength	Oil Yield (%w/w)	TLC observation
$Ca(OCH_3)_2$	3% 5% 7%	42.6 36.11 37.96	
MgO	3% 5% 7%	33.31 14.55 15 (Gel)	

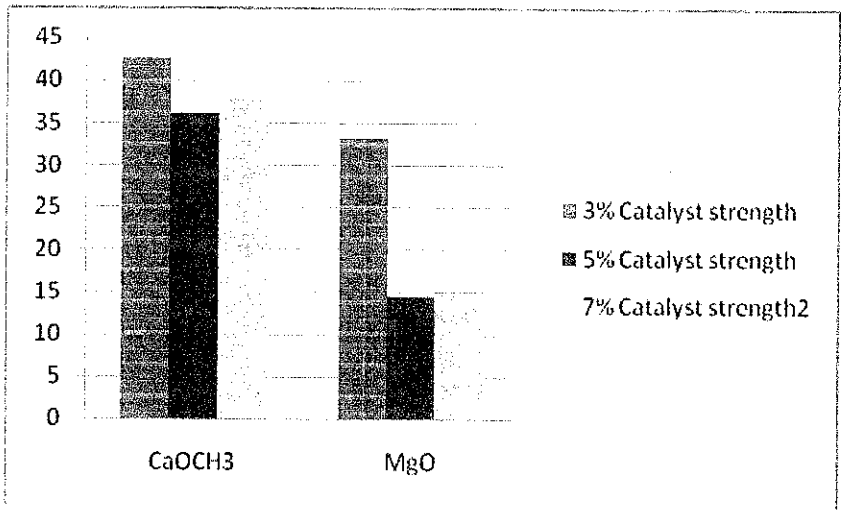


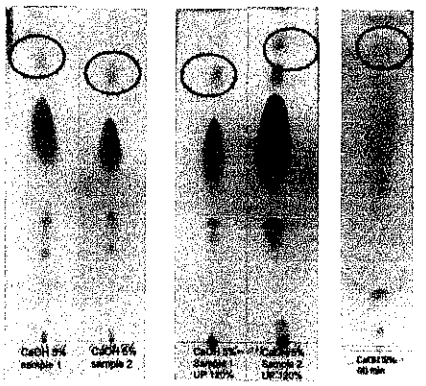
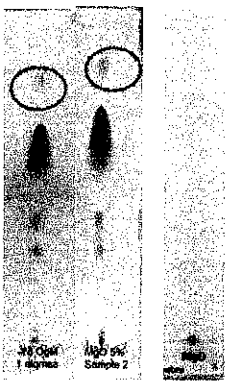
Figure 4.3: Oil Yield (%w/w) versus catalyst type and catalyst strength

From table 4.4 and figure 4.2, shown that $Ca(OCH_3)_2$ catalyst were better both in oil yielded percentage and biodiesel conversion, compared to MgO catalyst. Although the use of MgO catalyst shown significant oil yield and biodiesel conversion, the possibilities of producing gel or emulsified oil still exist. Meanwhile using $Ca(OCH_3)_2$ as catalyst had shown increased biodiesel conversion with increased catalytic strength. From this experiment, catalytic activity increased with increase catalyst strength for $Ca(OCH_3)_2$ and vice versa for MgO. The increased in catalytic strengths is explained by increased basicity of the solution. The more basic the solution is favor in transesterification process to the extent of the catalyst amount not poisoning the system. As for MgO, study by Gryglewiz (1999) found that the catalyst exhibit very low catalytic activity compared to CaO. This shown the catalytic increase with decrease order of group 1 metal in periodic table. For this experiment, catalyst strength at 3% is the best parameter.

4.5 In-situ transesterification using ultrasound water bath (Effect of ultrasonic power)

In this experiment, the transesterification processes were carried out using Transsonic Digital Ultrasonic water bath at 40% and 120% ultrasonic power. $Ca(OCH_3)_2$ and MgO at 5% catalyst strength were used with other parameters keep constant as previous experiment. The result is as table 4.5 and figure 4.3.

Table 14: Oil yield and observation at different ultrasonic power

Catalyst	Ultrasonic Power (%)	Oil Yield (%w/w)	TLC observation
$Ca(OCH_3)_2$	40% (Sample 1) 40% (Sample 2) *Average* *Standard deviation* 120% (Sample 1) 120% (Sample 2) *Average* *Standard deviation* *Previous data* 80%	23.91 23.76 *23.83* 0.21 27.7 20.96 *24.33* 3.45 36.11	 40% 120% 80%
MgO	40% (Sample 1) 40% (Sample 2) *Average* *Standard deviation* 120% (Sample 1) 120% (Sample 2) *Average* *Standard deviation* *Previous data* 80%	11.41(gel) 17.20(gel) *14.31* 2.89 12.84 (wax) 6.41 (wax) *9.63* 3.21 14.55 (wax)	 40% 80%

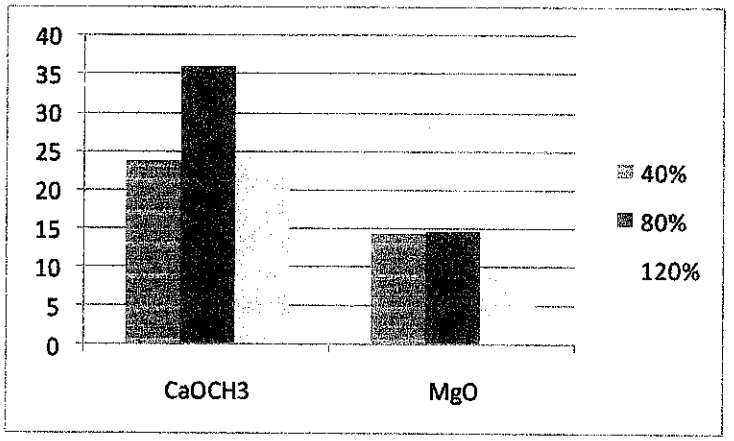


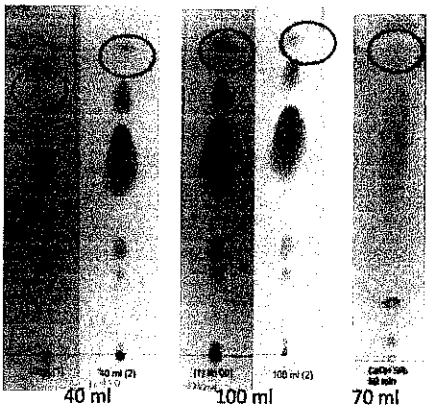
Figure 4.4: Oil Yield (%w/w) versus catalyst type and ultrasonic power

For experiment using MgO as catalyst, all the end product having very low cloud point that is behave as gel-wax at room temperature. Thus TLC analysis for experiment at 120% ultrasonic power is not possible. As can be seen on MgO at 80% ultrasonic power TLC plate, no pattern is visualized due to wax formation. In term of oil yield percentages, by taking the average of samples there is not much different for 40% and 120% ultrasonic power, but using higher ultrasonic power is not economy efficient result from increase energy consumption. And the percentage of oil yield at 80% is much higher than the other two ultrasonic parameters. This might be because of adequate cavitations give better surface area to oil extracted to be in contact with catalyst active sites. Also as shown in figure 4.3, it is obvious MgO were outperformed by $Ca(OCH_3)_2$, both in oil yield percentage and biodiesel conversion. Thus MgO will not to be used in the next experiment. For this experiment, ultrasonic power at 80% is the best parameter.

4.6 In-situ transesterification using ultrasound water bath (Effect of alcohol/oil ratio)

The experiment aims to study the effects of reducing or increasing the amount of alcohol used in transesterification process. For a complete transesterification process, the molar ratio of alcohol to oil must be 3 to 1. In order to prevent reversible process path in transesterification, alcohol is used in excess about the ratio of 6 or more to oil in conventional biodiesel production. In this experiment, selection of alcohol ratio were based on ratio of solvent used in oil extraction, that is about at the ratio of 7 to 1 w/v ratio of raw material. The result of alcohol ratio study is as shown as table 4.6 and figure 4.4.

Table 15: Oil yield and observation at different alcohol molar ratio

Catalyst	Volume used (ml)	Alcohol Ratio (molar ratio)	Oil Yield (%w/w)	TLC observation
$Ca(OCH3)_2$	40 (Sample 1)	107:1	19.33	
	40 (Sample 2)	107:1	22.21	
	Average		*20.77*	
	Standard deviation		1.44	
	100 (Sample 1)	268:1	30.53	
	100 (Sample 2)	268:1	27.70	
	Average		*29.12*	
	Standard deviation		1.41	
	Previous data			
	70	188:1	36.11	

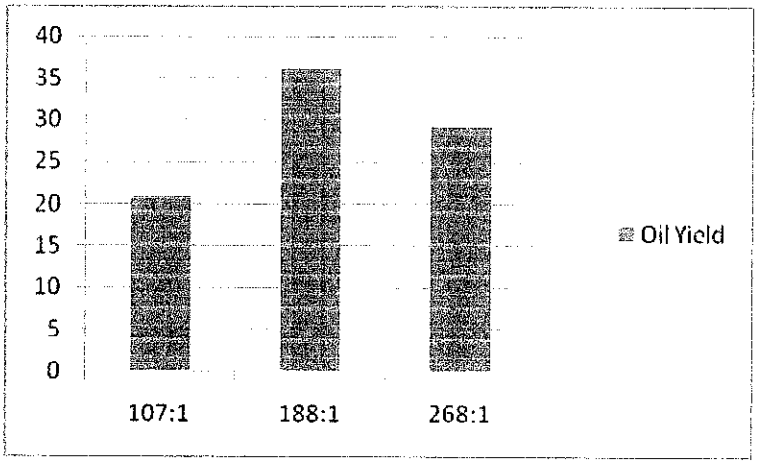


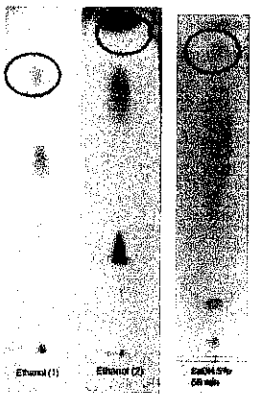
Figure 4.5: Oil Yield (%) versus alcohol molar ratio

The oil yield percentage data for 7:1 was better than the other two parameters. In term of biodiesel conversion, 10:1 sample 1 w/v ratio is the best. However the different is not significant compared to other variable parameters. For this experiment, it is concluded that in situ transesterification can be achieved even using 40 ml of alcohol (methanol) for every 10 gram raw materials. This support the claims made by Hielscher-Ultrasound Technology which stated the alcohol used can be reduced to 15% by the application of ultrasonic. Although the claim is for conventional biodiesel production using pre-extracted oil, it is believe to be valid for in-situ transesterification. The cavitations in ultrasonic give more surface contacts between the Jatropha seeds and the alcohol as solvent and also between the extracted oil and the alcohol. However, using more alcohol would not give any issue in term of economy efficiency, as un-reacted methanol still can be recovered, recycled and reused later. 188:1 molar ratio is selected to be the best parameter.

4.7 In-situ transesterification using ultrasound water bath (Effect of alcohol type: Ethanol)

These experiment aims to study the effect of using ethanol as alcohol instead of using methanol. Methanol is selected to be used in the research because it is commonly used and cheaper than other higher alcohols. Higher alcohols with increasing molecular weight however reported to improves the cold flow properties of the product, at the cost of a less efficient transesterification reaction. Initially, the experiment was conducted using $Ca(OCH_3)_2$ and MgO as catalyst. Sample containing MgO is dropped from observation as the product is very little wax particles and no oil at all, suggesting that MgO is not suitable to be used with Ethanol. The result and observation using $Ca(OCH_3)_2$ catalyst is as shown in table 4.7 and figure 4.5.

Table 16: Oil yield and observation at different alcohol type

Catalyst	Alcohol	Oil Yield (%w/w)	TLC observation
Ca(OCH3)2	Ethanol (Sample 1)	22.18	
	Ethanol (Sample 2)	23.96	
	Average	*23.08*	
	Standard deviation	0.89	
	Previous data	36.11	
	Methanol		

Ethanol Methanol

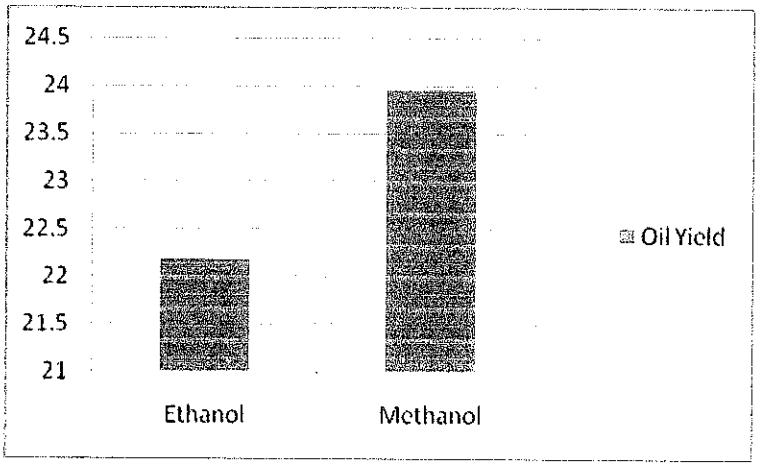


Figure 4.6: Oil Yield (%w/w) versus alcohol type

In this experiment, it is found that the oil percentage yield is way better when using Methanol as alcohol or solvent. These results however did not agreed with Haas et al (2004), Surya (2008), which found that Ethanol as solvent gave more oil yield than Methanol. The reason might be because of different catalyst use in the experiment, and the extraction capacity of the alcohols depends on the type of catalyst used. In term of biodiesel conversion, ethanol sample 2 found to have better biodiesel yield. However that is not the case for ethanol sample 1. From the finding of this experiment, methanol will continue to be used for proceeding experiment. But as Ethanol also previously reports to give better oil yield, the use of this alcohol should be assess in future study.

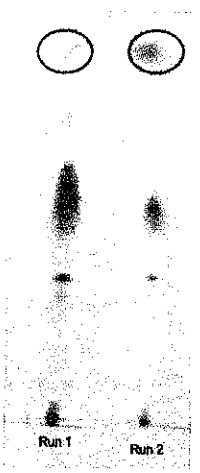
4.8 In-situ transesterification using ultrasound water bath (Catalyst reusability)

In this experiment, The parameters used were:

i. Weight of Ground Jatropha seeds: 50 gram
ii. Catalyst and Catalyst strength: $Ca(OCH_3)_2$ 5%
iii. Time: 60 minute
iv. Alcohol/Solvent: Methanol
v. Alcohol ratio: 4:1 %w/v
vi. Ultrasonic power: 120%
vii. Temperature: 60°

The sample from first run is filtered and re used in second run to study the catalyst activity, percentage of oil yield and biodiesel conversion if the raw material and catalyst is reused. The result and observation of the experiment is as shown in table 4.8.

Table 17: Oil yield and observation at first and second run best parameter

Catalyst	Alcohol	Oil Yield (%w/w)	TLC observation
Ca(OCH3)2	First run Second run	14.23 6.99	

From the result, the percentage of oil yield at first run is only 11.38%, which is considered to be much lowered than was expected. The possible reason of low yield of oil might be because of the amount of raw materials used which are more than previous experiment lead to saturated flask contents. Limitation of space in glassware (small round bottom flask) render the ultrasonic power less effective as less cavitations effects due to limited space in the flask. This in turn, will reduce the surface contacts between the raw materials, the solvent, and the catalyst. The biodiesel yielded however is acceptable. For second run experiment, the oil yield percentage is half of the first run, although it is small, the result shown that the raw material can always be reused to get the most oil contents in the raw materials. It is also shown the catalyst $Ca(OCH_3)_2$ to exhibit reusable abilities, and can be used several times until it is degrade. As can be seen in TLC observation, the different of biodiesel conversion is significant between first and second run. The second run found to be had better biodiesel conversion. This explained by lower oil yield, give better residence contact between the oil molecule and the catalyst active sites.

4.9 Transesterification using ultrasound water bath (conventional oil transesterification)

Pre extracted oil is used instead of using ground Jatropha seeds. Other parameters used were the same with previous experiment. This experiment is as standard references to compare between in-situ transesterification and conventional transesterification. The TLC plate observation is as shown in table 4.9.

Table 18: TLC observation for oil transesterification

Catalyst	Alcohol	TLC observation
Ca(OCH3)2	Sample 1 Sample 2	

As can be seen, it is found that there is complete conversion of biodiesel. As there is no pattern of triglyceride exist on the TLC plates. From this experiment, two conclusion can be made, the first one is $Ca(OCH_3)_2$ is a good catalyst giving complete biodiesel conversion. Secondly, the reaction in conventional method is better than in in-situ transesterification. This is however because of readily available vegetable permit rapid reaction at the start of experiment with addition to application of ultrasonic. This is not the case in in-situ transesterification as there is duration for oil to be extracted, and to be in contacted with catalyst and the solvent.

CHAPTER 5: CONCLUSION & RECOMMENDATION

5.1 Conclusion

Jatropha seeds are very promising raw materials to be used in biodiesel production. The fresh seeds not only yielding high amount of oils, it also having very low free fatty acid percentages which eligible the need of one stage transesterification, thus shorter biodiesel production duration time compared to others raw materials. Jatropha also easy to plant, it can grow with minimal attention even on the poor soil condition, and in return fertilizing the soils by its natural fertilizing effects. Although the oil content is not as much as palm oil, Jatropha is much preferable to be use a feedstock due to its inedible properties. Fresh palm oil which also feedstocks for cooking oil production will only lead to hiking of food prices as it is also used in food industry.

In-situ transesterification on the other hand had proven to give lower biodiesel production duration time. This is because in in-situ transesterification, the time need to pre extracted the oil is eliminated. In in-situ transesterification, alcohol is used both as extraction solvent and transesterification reagent thus provide pure products and save the production cost. However in the research experiment, the oil yield by in situ transesterification method still lower compared to the amount of oil yielded in Soxhlet extraction method. Although this can be solve by running the filtered used feedstock for the second time, it is still not feasible as it is time consuming. Thus future study should be done to address the issue by varying the type of solvent/alcohol used.

The application of ultrasonic also has proven to speed up the reaction time for biodiesel conversion. This is because the existence of physical cavitations of bubbles provides the kinetic energy needs for maximum surface contact between raw materials and solvent, and between extracted oil and alcohols. Event at low ultrasonic frequency, the extraction and reaction is still occurring. In oil transesterification experiment, the visual on TLC plate shows the complete conversion of triglyceride to biodiesel in 60 minute only.

Beside in-situ transesterification and ultrasonic application, the uses of heterogeneous catalyst also benefit the biodiesel production. Out of five type of heterogeneous catalyst selected to be study in the experiment, two which is Calcium Methoxide and Magnesium Oxide shown catalytic activity need for biodiesel conversion. Magnesium Oxide however not be used throughout all the experiment, because it is more prompt to give gel products compared to Calcium Methoxide. Reducing the catalyst strengths and using bigger sizes of particles might help eliminate this issue. Heterogeneous also can be reusable and less likely to form soaps which in turn lead to simple purification process. Zero formation of soaps meant improved product yield and purity. From the research work, the best parameter is identified. The parameters can be further to be assessed or can be used as starting point for future project work.

5.2 Recommendation for future works

The finding of research project and the experiment conducted has succeeded in suggesting the parameters need for optimum condition in biodiesel production. Nevertheless, there is always space for improvement, thus some recommendation should be look on for future works.

i. Investigate other effect of heterogeneous catalyst. In term of its group, alkaline earth metal hydroxides, oxides or alkoxides. Knowing which group giving the best performances enables deeper study to be on the catalysts from the group specifically.
ii. Extend the heterogeneous catalyst study to catalyst characterization. Catalyst characterization study provides information on the performances of the catalyst used. As example the relation of pore surface to catalyst activity.
iii. Investigate the time study for each of experiment with multiple runs for every experiment to find most accurate results. Extra stocks of raw materials need to ensure this.
iv. Analyzes all the products in every experiment using gas chromatography for accurate oil composition data and to find the exact biodiesel percentage.
v. More variation in variable parameter study ranges selection to find the most accurate data presentation for relation of the parameter at one value to other.
vi. Acquire enough high purity biodiesel for analytical study. This is to compare the biodiesel produced whether it is following the biodiesel ASTM standard or not.

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APPENDICES

ASTM REQUIREMENT

Property	Method	Limits	Units
Flash point	D 93	130 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity at 40°C	D 445	1.9 – 6.0	mm^2/s
Sulfated ash	D 874	0.020 max	wt.%
Total sulfur	D 5453	0.05 max	wt.%
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report	°C
Carbon residue	D 4530	0.050 max	wt.%
Acid number	D 664	0.80 max	mg KOH/g
Free glycerine	D 6584	0.020	wt.%
Total glycerine	D 6584	0.240	wt.%
Phosphorus	D 4951	0.0010	wt.%
Vacuum distillation end point	D 1160	360°C max, at 90% distilled	°C

Property	Units	Lower limit	Upper limit	Test-Method
Ester content	% (m/m)	96.5	–	Pr EN 14103d
Density at 15°C	kg/m^3	860	900	EN ISO 3675 / EN ISO 12185
Viscosity at 40°C	mm^2/s	3.5	5.0	EN ISO 3104
Flash point	°C	>101	–	ISO CD 3679e
Sulfur content	mg/kg	–	10	–
Tar remnant (at 10% distillation remnant)	% (m/m)	–	0.3	EN ISO 10370
Cetane number	–	51.0	–	EN ISO 5165
Sulfated ash content	% (m/m)	–	0.02	ISO 3987
Water content	mg/kg	–	500	EN ISO 12937
Total contamination	mg/kg	–	24	EN 12662
Copper band corrosion (3 h at 50°C)	rating	Class 1	Class 1	EN ISO 2160
Oxidation stability at 110°C	hours	6	–	pr EN 14112k
Acid value	mg KOH/g	–	0.5	pr EN 14104
Iodine value	–	–	120	pr EN 14111
Linoleic acid methyl ester	% (m/m)	–	12	pr EN 14103d
Polyunsaturated (≥ 4 double bonds) methylester	% (m/m)	–	1	–
Methanol content	% (m/m)	–	0.2	pr EN 141101
Monoglyceride content	% (m/m)	–	0.8	pr EN 14105m
Diglyceride content	% (m/m)	–	0.2	pr EN 14105m
Triglyceride content	% (m/m)	–	0.2	pr EN 14105m
Free glycerine	% (m/m)	–	0.02	pr EN 14105m / pr EN 14106
Total glycerine	% (m/m)	–	0.25	pr EN 14105m
Alkali metals (Na + K)	mg/kg	–	5	pr EN 14108 / pr EN 14109
Phosphorus content	mg/kg	–	10	pr EN14107p

Raw material oil contents comparison and Jatropha properties

Sample	16:0	16:1	18:0	18:1	18:2	18:3	Others
Cottonseed	28.7	0	0.9	13.0	57.4	0	0
Poppyseed	12.6	0.1	4.0	22.3	60.2	0.5	0
Rapeseed	3.8	0	2.0	62.2	22.0	9.0	0
Safflowerseed	7.3	0	1.9	13.6	77.2	0	0
Sunflowerseed	6.4	0.1	2.9	17.7	72.9	0	0
Sesameseed	13.1	0	3.9	52.8	30.2	0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Wheat grain[a]	20.6	1.0	1.1	16.6	56.0	2.9	1.8
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Corn marrow	11.8	0	2.0	24.8	61.3	0	0.3
Castor[b]	1.1	0	3.1	4.9	1.3	0	89.6
Tallow	23.3	0.1	19.3	42.4	2.9	0.9	2.9
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	0
Bay laurel leaf[c]	25.9	0.3	3.1	10.8	11.3	17.6	31.0
Peanut kernel[d]	11.4	0	2.4	48.3	32.0	0.9	4.0
Hazelnut kernel	4.9	0.2	2.6	83.6	8.5	0.2	0
Walnut kernel	7.2	0.2	1.9	18.5	56.0	16.2	0
Almond kernel	6.5	0.5	1.4	70.7	20.0	0	0.9
Olive kernel	5.0	0.3	1.6	74.7	17.6	0	0.8
Coconut[e]	7.8	0.1	3.0	4.4	0.8	0	65.7

* xx:y: xx number of carbon atoms; y number of double bonds

[a] Wheat grain oil contains 11.4% of 8:0 and 0.4% of 14:0 fatty acids

[b] Castor oil contains 89.6% ricinoleic acid

[c] Bay laurel oil contains 26.5% of 12:0 and 4.5% of 14:0 fatty acids

[d] Peanut kernel oil contains about 2.7% of 22:0 and 1.3% of 24:0 fatty acids

[e] Coconut oil contains about 8.9% of 8:0, 6.2% 10:0, 48.8% of 12:0, and 19.9% of 14:0 fatty acids

Table 2 – Physical and mechanical properties of Jatropha curcas L. fruits, nuts, and kernels.

Properties	N		Fruit	Nut	Kernel
1000-unit mass, g	100		14560.9 + 2415.4	1322.4 + 14.6	688.1 + 5.7
Nut fraction, %	3	24.53			
Kernel fraction, %	3	12.63			
Shell fraction, %	3	11.90			
Hull fraction, %		75.47			
Length, mm	100		33.36 + 1.58	21.02 + 1.03	15.45 + 0.54
Equatorial width perpendicular to the length, mm	100		30.05 + 1.08	9.58 + 0.28	7.42 + 0.33
Breadth perpendicular to the length and width, mm	100		31.51 + 0.97	11.97 + 0.30	10.25 + 0.36
Geometric mean diameter, mm	100		31.60 + 1.01	13.40 + 0.36	10.55 + 0.34
Sphericity	100		0.95 + 0.03	0.64 + 0.03	0.68 + 0.01
Bulk density, g/cm^3	3		0.47 + 0.00	0.45 + 0.01	0.42 + 0.01
Solid density, g/cm^3	20		0.95 + 0.02	1.04 + 0.04	1.02 + 0.05
Porosity, %	NA		50.53	56.73	58.82
Surface area, mm^2	100		3139.21 + 197.41	534.12 + 31.81	306.48 + 22.08
Specific surface area, cm^2/cm^3	100		0.90 + 0.07	1.91 + 0.12	2.12 + 0.08
Coefficient of static friction on various surfaces					
Ply wood	3		0.50 + 0.05	0.49 + 0.03	0.72 + 0.06
Steel	3		0.64 + 0.05	0.46 + 0.01	0.73 + 0.03
Stainless steel	3		0.46 + 0.02	0.49 + 0.04	0.65 + 0.02
Angle of repose, °					
Filling method	3		53.53 + 1.72	54.00 + 5.13	60.23 + 6.16
Emptying method	3		42.91 + 0.67	37.76 + 2.85	42.92 + 0.82
Rupture force, N	20		135.39 + 54.86	146.63 + 14.82	67.72 + 19.03
Deformation at rupture point, mm	20		4.36 + 1.42	2.10 + 0.19	1.74 + 0.37
Deformation ratio at rupture point	20		0.15 + 0.05	0.22 + 0.02	0.23 + 0.05
Hardness, N/mm	20		30.58 + 5.88	69.98 + 6.22	38.52 + 5.59
Energy used for rupture, N mm	20		300.88 + 237.84	124.44 + 19.95	51.61 + 26.84

n is the number of samples. Data are mean values + standard deviation. NA is not applicable.